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INFLUENCE OF THE SOLVENT ON THE ELECTROMOTIVE FORCE OF SILVER–SILVER HALIDE CELLS

BY ALEXIS S. AFANASIEV

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Introduction

Many investigations in recent years have given ample justification for the extension of Nernst's osmotic theory and the ordinary laws of thermodynamics to non-aqueous solutions. On this basis A. E. Brodsky[1] has given a formula for the change in electromotive force (e. m. f.) with solvent for the cell

$$M \mid MX, M'X(c_1) \mid M'Y(c_2), MY \mid M$$

in two solvents (M, metal; MX and MY, slightly soluble salts (depolarizators) of the metal; M'X and M'Y, very soluble salts; $c_1 = c_2$, equal concentrations of the salts). Brodsky's formula

$$E - E' = \frac{RT}{nF} \ln \frac{L_1\nu_1 \times L_2'\nu_2'}{L_1'\nu_1' \times L_2\nu'_2} \tag{1}$$

in which E and E' represent the e. m. f.'s of the cell in Solvents I and II, and L and ν are the solubilities and activity coefficients of the salts M'X and M'Y in saturated solutions in Solvents I and II. In saturated solutions in the different solvents the relationships $\nu_{M'X} = \nu'_{M'X}$ and $\nu_{M'Y} = \nu'_{M'Y}$ are approximately true. This has been demonstrated for α in the classic theory by Walden and van Laar,[2] and then

$$E - E' = \frac{RT}{nF} \ln \frac{L_1 \times L_2'}{L_1' \times L_2} \tag{2}$$

This formula is a consequence of the general formula given by Brodsky,[1] and has been deduced thermodynamically through a series of two cycles relating the free energy of reaction both in solution and without solvent, the initial activities and the activities of salts in saturated solutions. The

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[1] Brodsky, Z. *physik. Chem.*, *121*, 126 (1926); Z. *Elektrochem.*, 32, *5* (1926); "Scientific Magazine of the Chemical Catheder of Katerinoslaw," 1926, Vol. I; *Physik. Z.*, 35, 665 (1929).

[2] Walden, Z. *physik. Chem.*, 55, 683 *(1906);* van Laar, *ibid.*, 58, 571 (1907).

equilibrium in solution may be calculated from thermal data by means of these cycles. Formula 2 may be applied only in dilute solutions. Professor Brodsky has demonstrated the correctness of this formula, using the cell

$$\mathrm{Hg} \mid \mathrm{Hg_2Cl_2},\ \mathrm{KCl}\ (c_1) \mid \mathrm{KBr}\ (c_2),\ \mathrm{Hg_2Br_2} \mid \mathrm{Hg}$$

and suggested to the writer the problem of applying the formula to the cell

$$\mathrm{Ag} \mid \mathrm{AgCl},\ \mathrm{KCl}\ (c_1) \mid \mathrm{KBr}\ (c_2),\ \mathrm{AgBr} \mid \mathrm{Ag}$$

in ethyl alcohol–water and methyl alcohol–water mixtures, using various concentrations of potassium chloride and bromide.

Experimental

The potentials of the Ag–AgCl and Ag–AgBr electrodes vary considerably depending on the methods of preparation, as has been shown by numerous investigators during the last thirty-five years. For example, the e. m. f. of the cell

$$\mathrm{Ag} \mid \mathrm{AgCl},\ \mathrm{KCl}\ (1\ M) \mid \mathrm{KCl}\ (1\ M),\ \mathrm{Hg_2Cl_2} \mid \mathrm{Hg}$$

in water at 25° has been measured by a number of workers since 1917, and has given values of E varying from +0.0422 to +0.0467.[3] Further data have been presented by Bronsted[4] and by Abegg and Cox.[5] The theoretical value given by Lewis and Randall[6] is $E = 0.0466$ v. These differences may be ascribed to the lack of a uniform method of electrode preparation. The variable manipulatory and thermal conditions under which silver and its halides are prepared have a marked effect on the characteristics of the surfaces of the products and, as a result, the silver has different solution tensions ("elektrolytische Lösungstension" of Nernst) and the halides differ in solubility. These points have been discussed in detail by Lewis, Randall, and others.[7]

In the early part of this work, electrolytically coated silver–silver halide electrodes were used, prepared according to the directions of Goodwin, Jahn and Halla.[8] A pure white silver layer was prepared by electrolysis on a carefully cleaned platinum wire. The electrolysis lasted for five to six days and

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[3] Noyes and Ellis, THIS JOURNAL, **39**, 2532 (1917), give E = 0.0438 v.; R. Gerke, ibid., 44, 1684 (1922), E = 0.0458 v.; Scatchard, *ibid.*, 47,648,696 (1925), *E* = 0.0-266 v ; Nonhebel and Hartley, *Phil. Mag.*, [6] 50, 729 (1925), E = 0.0467 v.; Randall and Young, THIS JOURNAL, 50, 989 (1928), E = 0.455 v.; Mazee, *Trans. Am. Electrochem. Soc.*, (1929), using different methods of preparation, E = 0.0422, 0.0442, 0.0444, 0.0466 v.

[4] Bronsted, *Z. physik. Chem.*, 50, 481 (1905).

[5] Abegg and Cox, *ibid.*, 46, 1 (1903).

[6] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw–Hill Book Co., Inc., New York, 1923, pp. 335, 407.

[7] Lewis, THIS JOURNAL, 28, 158 (1906); MacInnes and Parker, *ibid.*, 37, 1447 (1915); Guntelberg, Z. *physik. Chem.*, **123**, 198 (1926); Randall and Young, Ref. 3; Mazee, Ref. 3; Carmody, THIS JOURNAL, 51, 2901 (1929).

[8] Goodwin, *Z. physik. Chem.*, 13, 577 (1894); Jahn, *ibid.*, 33, 545 (1900); Halla, *Z. Elektrochem.*, 17, *179 (1911).*

was carried out in a $KAg(CN)_2$ solution containing an excess of KCN, using a current density of **0.9** milliampere per sq. cm., with 15-20 electrodes in each set. The electrolyte was prepared as directed by Ullmann.[9] The electrodes were not protected from diffused daylight. After completion of the electrolysis, they were soaked in distilled water for one or two days, then immersed in a dilute silver nitrate solution and short-circuited to eliminate occasional differences in potential. The electrodes were then coated with a layer of silver halide by electrolysis **as** anodes in **0.75** M hydrochloric or hydrobromic acid, with a current density of **0.2** milliampere per sq. cm. The electrolysis was carried out in complete darkness and lasted for five to six hours. After completion the electrodes were placed in dilute potassium chloride or bromide solution, short-circuited and kept in the dark.

Despite the careful preparation, these electrodes were reproducible only to within 0.1–0.2 mv., whereas other investigators have prepared electrodes of this type reproducible to within 0.01–0.5 mv.[10] It seems that the reproducibility of electrodes of this type depends upon many factors which are either accidental or imperceptible. Carmody[10] has noted the influence of the absorption of cyanide ion and of exposure to daylight, both of which may be possible explanatory factors. Since the reproducibility of this type of electrode was unsatisfactory, they were used only in the early part of the work (water and ethyl alcohol–water solutions).

Subsequent work was carried out with electrodes of the type recommended by Noyes and Ellis[3] and by Lewis.[7] This type differs from that of Goodwin and Jahn in that the electrolytic layer is replaced by a silver sponge produced by thermal decomposition of silver oxide on the silvered platinum. The method of halogenizing was the same as before. The electrodes as prepared differed by about **0.01** mv. both in water and alcohol solution. Other workers[11] have obtained a reproducibility of **0.00–0.25** mv.

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[9] Ullmann, "Enzyklopadie der technischen Chemie," "Starke Versilberung."

[10] Goodwin, Ref. 8, 0.1–0.2 mv.; Jahn, Ref. 8, several tenths of a mv.; Sackur, *Z. physik. Chem.*, 38, 128 (1901), 0.01–0.02 mv.; Bronsted, Ref. 4, 0.1–0.5 mv.; Byron, *J. Russ. Phys.-Chem. Soc.*, 39, 1506 (1907), 0.00–0.02 mv.; Byron and Boris Afanasiev, *ibid.*, 40, 70 (1908); 41, 1175 (1909), 0.03 mv.; Drucker, *Z. Elektrochem.*, 18, 562 (1912), 0.5 mv.; MacInnes and Parker, Ref. 7, several tenths of a mv.; MacInnes and Beattie, THIS JOURNAL, 42, 1117 (1920), 0.03–0.05 mv., but from divers series 0.1–0.2 mv.; Nonhebel and Hartley, Ref. **3,** 0.02 mv.; Güntelberg, Ref. 7, several tenths of a mv.; Carmody, Ref. **7,** 0.02 in one series. Other work with this type of electrode has been reported by Thiel, *Z. anorg. Chem.*, 24, 1 (1900); Abegg and Cox, Ref. 5; Pearce and Hart, THIS JOURNAL, 43, **2483** (1921); Sheppard and Elliot, *Science,* 56, 578 (1922); Randall and Young, Ref. **3;** Horsch, THIS JOURNAL, 41, 1787 (1919); Mazee, Ref. **3.**

[11] Güntelberg, Ref. 7, 0.02–0.2 mv.; Noyes and Ellis, Ref. 3, 0.05 mv.; Mazee, Ref. **3,** 0.00 mv. Other workers with this type of electrode have been Harned and Fleysher, THIS JOURNAL, 47, 82 (1925); Harned and Douglas. *ibid.*, 48, 3095 (1926); Harned and Brumbaugh, *ibid.*, 44, 2729 (1922); Harned and Robinson, *ibid.*, 50, 3157 (1928); Lucasse, *ibid.*, 47, 743 (1925); *ibid.*, 51, 2598, 2605 (1929); Randall and Young, Ref. **3.**

with this type of electrode. The writer also replaced the electrolytically silvered platinum spiral with unsilvered spirals of pure silver, but the potential was not changed.[12]

The type of electrode recommended by Noyes and Ellis is definitely to be preferred. The third type, similar to the Hg–Hg_2Cl_2 electrode is of no particular interest. The electrodes were protected from actinic light during and after halogenizing, and the measurements were carried out by the light of a dark yellow incandescent lamp. Each type of electrode was used exclusively in half of the work, the Goodwin–Jahn type in the first half and the Noyes–Ellis type in the last half; this necessitated great care in washing the electrodes whenever the solutions were changed. The apparatus was as usual: wire bridge, Weston normal cell, galvanometer (sensitive to 10^{-9} ampere). The apparatus was not thermostated, since the temperature variation was not over 0.1–0.2° during a series of measurements, corresponding to a difference in measured e. m. f. of less than the experimental error (about 0.03 mv.). The precision of the e. m. f. measurements was about 0.1–0.2 mv. All materials and reagents were chemically pure and many times crystallized (the potassium chloride, for example, was 99.85% pure). The solvents were prepared from Kahlbaum's "Methanol zur Analyse" and from C. P. ethyl alcohol. The electrodes were prepared in the same way both in water and alcohol, and the compositions are given in "gewicht prozent."

Results

The e. m. f. values given are the average of three measurements on three different pairs of electrodes, the separate values differing from one another by not more than 0.1–0.3 mv. The temperature coefficients were measured approximately at 15–30°.

TABLE I

TEMPERATURE COEFFICIENT DATA

		Ethyl alcohol		Methyl alcohol	
Solvent	Water	24.67%	50 60%	26.32%	45.03%
dE/dT, v.	−0.00018	−0 00017	−0.00012	−0.00017	−0.00014

No correction was made for diffusion potential since the mobilities of Cl^- and Br^- are practically the same in equal concentrations of potassium chloride or bromide, and they are unknown for water–alcohol mixtures. No activity correction is necessary, since the activities of Cl^- and Br^- are almost identical in equal concentrations of the potassium salts.[13]

One point which should be noted is the systematic decrease of e. m. f. as the concentration is diminished, notwithstanding that c_{KCl} remains equal to c_{KBr}. This same effect was observed by A. E. Brodsky[14] on the cell

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[12] See also Randall and Young, Ref. **3**.

[13] Harned, THIS JOURNAL, 51, 416 (1929).

[14] Brodsky, *Z. Elektrochem.*, 32, 5 (1926), and Ref. 1.

$$\mathrm{Hg} \mid \mathrm{Hg_2Cl_2},\ \mathrm{KCl}\ (c_1) \mid \mathrm{KBr}\ (c_2),\ \mathrm{Hg_2Br_2} \mid \mathrm{Hg}$$

The writer has made the same observation on the same cell at concentrations of **0.1** to **0.0001 M.** The value found for the e. m. f. may be compared with Goodwin's results. Goodwin measured the e. m. f. of the cell

$$\mathrm{Ag} \mid \mathrm{AgCl},\ \mathrm{KCl}\ (c_1) \mid \mathrm{KBr}\ (c_2),\ \mathrm{AgBr} \mid \mathrm{Ag}\ (c_1 = c_2)$$

and found in water an e. m. f. of **0.148** mv. at 25° (c = **0.1 M), 0.149** v. (c = 0.05 M). Must be **0.150** v. at 15° (c = **0.1 M), 0.151** v. (c = **0.05** *M*). The writer's measurements at 15° give an e. m. f. of **0.1533** v. at $c = 0.1\ M$ and **0.1528** v. (interpolated) at c = **0.05 M.** The discrepancy is explainable on the basis of insufficient precision in Goodwin's measurements made in 1894, since his individual observations at the same concentration and temperature differed by 4–6 mv. The observed increase of e. m. f. with diminishing concentration is easily accounted for on this basis.

TABLE II

RESULTS

Solvent	Concentration KCl	Concentration KBr	t, °C.	*E* at this t, volt	*E* corrected at 15°, volt
Water	0.10010	0.10008	18.7	0.1528	0.1533
Water	.01006	.01006	18.6	.1514	.1519
Water	.00100067	.00100064	10.5	.1515	.1507
Ethyl alcohol, 24.67%	.10011	.10011	15.1	.1469	.1469
	.01006	.01006	15.2	.1447	.1447
	.001013	.001081	15.9	.1419	.1421
50.6%	.10012	.10007	16.8	.1392	.1394
	.01006	.01006	16.5	.1371	.1374
	.001011	.001011	16.6	.1344	.1346
75.06%	.050053	.050055	15.0	...	.1307
	.0050305	.0050307	15.0	...	.1294
Methyl alcohol, 26.32%	.100062	.100069	9.9	.1463	.1455
	.010058	.010059	10.2	.1455	.1446
45.03%	.100059	.100025	14.2	.1400	.1399
	.010056	.010053	14.5	.1387	.1386
74.72%	.100015	.100011	16.5	.1313	.1315
	.010049	.010049	16.6	.1307	.1309
99.69%	.010007	.010008	15.7	.1245	.1247

Verification of **the** Theory.—The e. m. f. values obtained were used in verifying Formula 2. Solubility data were taken from the work of S. **Zeitlin.**[15] Table III gives the observed e. m. f. values and those calculated with the aid of Formula **2.** Column **1** lists the first solvent, for which the e. m. f. (E) is known, and Column 2 gives the second solvent, for which the e. m. f. (*E*′) has been measured and calculated from E and the solubilities. E and *E*′ correspond to the same concentrations; t is 15°; the e. m. f. values are rounded to millivolts and the solvent compositions are given to even

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[15] S. Zeitlin, *Z. physik.* Chem., 121, 39 (1926).

percentages. Values in parentheses are interpolated from closely adjacent concentrations.

TABLE III

RESULTS

Solvent I	Solvent II	$E-E'$, calcd.	0.1 M E', calcd.	E', meas.	A, %	0.05 M E', calcd.	E', meas.	Δ, %
Water	EtOH, 25%	0.0054	0.148	0.147	1	(0.147)	(0.146)	1
Water	EtOH, 50%	.0118	.141	.139	1.5	(.141)	(.139)	1.5
Water	EtOH, 75%	.0184	..	..	...	(.134)	.131	2
EtOH, 25%	EtOH, 50%	.0064	.140	.139	1	(.140)	(.139)	1
EtOH, 25%	EtOH, 75%	.0129			...	(.133)	.131	2
EtOH, 50%	EtOH, 75%	.0065			...	(.132)	.131	1.5
Water	MeOH, 26%	.0041	.149	.145	3	(.149)	(.145)	2.5
Water	MeOH, 45%	.0098	.143	.140	3	(.143)	(.140)	2.5
Water	MeOH, 75%	.0153	.138	.131	5	(.137)	.131	4.5
Water	MeOH, 100%	.0204			...	..	..	...
MeOH, 25%	MeOH, 45%	.0057	.140	.140	0	(.139)	(.139)	0
MeOH, 25%	MeOH, 75%	.0111	.135	.131	2	(.134)	.131	2
MeOH, 25%	MeOH, 100%	.0163	..	..	...	..	..	...
MeOH, 45%	MeOH, 75%	.0055	.135	.131	2	(.134)	.131	2
MeOH, 45%	MeOH, 100%	.0174						
MeOH, 75%	MeOH, 100%	.0051						

Solvent I	Solvent II	0.01 M E', calcd.	E', meas.	A, %	0.005 M E, calcd.	E, meas.	A, %	0.001 M E, calcd.	E, meas.	A, %
Water	EtOH, 25%	0.147	0.147	0	(0.146)	(0.144)	1.5	0.145	0.142	2
Water	EtOH, 50%	.140	.137	2	(.140)	(.137)	2	.139	.135	3
Water	EtOH, 75%	.133	.130	2.5	(.133)	.129	2.5	..	..	.
EtOH, 25%	EtOH, 50%	.138	.137	0.5	(.138)	(.137)	1	.136	.135	1
EtOH, 25%	EtOH, 75%	.132	.130	0.5	(.131)	.129	1		..	.
EtOH, 50%	EtOH, 75%	.131	.130	1	(.130)	.129	0.5			
Water	MeOH, 26%	.148	.145	2	..	..	...			
Water	MeOH, 45%	.142	.139	2.5	..	..	...		..	.
Water	MeOH, 75%	.137	.131	4	..	..	...		..	.
Water	MeOH, 100%	.131	.125	5	..	..	...			
MeOH, 25%	MeOH, 45%	.139	.139	0	..	..	...			
MeOH, 25%	MeOH, 75%	.133	.131	1	..	..	...			
MeOH, 25%	MeOH, 100%	.128	.125	3	..	..	...			
MeOH, 45%	MeOH, 75%	.133	.131	1	..	..	...			
MeOH, 45%	MeOH, 100%	.121	.125	−2.5	..	..	...			
MeOH, 75%	MeOH, 100%	.126	.125	1	..	..	...			

The average deviation between $E'_{\text{meas.}}$ and $E'_{\text{calcd.}}$ is about 1.8%. These differences may be due to the somewhat uncertain values for the solubilities in the concentrated alcohols (the absolute values are not very large) The observed data demonstrate the validity of Formula 2 and its premises. A comparison of these results with recent data obtained in this Laboratory[16] indicates the correctness of the premises and shows that Nernst's osmotic

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[16] Brodsky arid Trachtenberp, *Z. physik.* Chem , **143A, 287 (1929);** Brodsky **and** Boruhowich, J. *chim. phys* , *26,* 542 **(1929).**

theory is applicable to the usual electrodes as well as to oxidation–reduction electrodes.

The writer wishes to express his thanks to Professor A. E. Brodsky both for suggesting the problem and for help in carrying it out. Part of the material presented appeared in *Z. Elektrochem.*, **39,** 220 (1929). Slight corrections are necessary to part of the published data; the corrections have been applied in this report.

Summary

1. The methods of preparation of silver–silver chloride and silver–silver bromide electrodes have been studied, and it has been found that the procedure recommended by Noyes and Ellis is to be preferred.

2. Measurements have been made of the e.m.f. of the cell Ag | AgCl, KCl (c_1) | KBr (c_2) ($c_1 = c_2$), AgBr | Ag in water and in ethyl and methyl alcohol–water mixtures of various concentrations.

3. The results obtained justify the application of Nernst's osmotic theory to non-aqueous solutions, as has been carried out by Professor A. E. Brodsky.

DNIEPROPETROVSK, EKATERINOSLAW, U. S. S. R.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, CAMBRIDGE, ENGLAND, AND THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PROPERTIES OF SELENIUM TETRACHLORIDE[1]

BY J. H. SIMONS

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The tetrahalogen compounds of the electronegative elements in group number six of the periodic table are of considerable interest from the point of view of molecular structure. On the Lewis theory the central atom should be represented with a shell of ten electrons, four pair of which are shared with the halogen atoms and one pair which is not shared. Henley and Sugden[2] propose a shell of eight electrons with two of the halogen atoms held by single electron bonds.

Of these compounds the following are known: SCl_4, SF_4, $SeBr_4$, $SeCl_4$, SeF_4, TeI_4, $TeBr_4$ and $TeCl_4$. The formulas of most of these have, however, been assigned from only an analysis of the crystalline compound. The molecular weights and therefore the number of atoms in the molecule have not been determined. In fact, a number of these compounds are very unstable crystalline substances, the crystal structures of which are not known. The stability of these compounds increases in the expected man-

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[1] Part of this work was done while the author was a National Research Fellow at Cambridge University.

[2] Henley and Sugden, *J. Chem. Soc.*, **1058** (1929).

ner as one proceeds from the iodide to the fluoride and also as one changes the central atom from sulfur to tellurium. SI_4, SBr_4 and SeI_4 are not known, undoubtedly because they are too unstable to exist under any ordinary laboratory conditions. SCl_4, $SeBr_4$ and TeI_4 are known only as very unstable solids which decompose upon heating. $SeCl_4$ and $TeBr_4$ are crystalline solids which can be sublimed. SF_4, SeF_4 and $TeCl_4$ form liquids under ordinary pressures. TeF_4 would be expected to be a stable compound but it has not yet been isolated.

Before these compounds can be used in a discussion of molecular structure, it is necessary that more information be obtained about them. In this paper a report of a study of selenium tetrachloride will be given.

Several attempts have been made to determine the molecular weight of selenium tetrachloride. Clausnitzer[3] reports that the vapor density by the Dumas method is one-half the normal value for $SeCl_4$ but does not record the temperature of the determination. Evans and Ramsay,[4] however, found the vapor density normal below 200° and the material half decomposed at 288°. Chambrie[5] finds the vapor density at 360° to be one-half normal. Beckmann[6] determined the freezing point lowering of selenium tetrachloride in acetic acid at 16.5' and obtained molecular weights varying from 142 to 152 depending on the concentration. He made very modest claims for these determinations, for he accounted for the results by a reaction with the solvent, a dissociation of the selenium tetrachloride, or a reaction with water in the solvent.

Preparation of Selenium Tetrachloride.—Elementary selenium was treated with pure dry chloride in a pyrex glass apparatus, which consisted of several tubes sealed into one another. The selenium was placed in the first tube, the air in the apparatus was flushed out with chlorine, and then the tube containing the selenium was placed in a small electric furnace. By proper control of the temperature the tetrachloride could be sublimed into the first tube out of the furnace, at the same time that a chlorine stream entered the tube in the furnace. When all of the selenium had reacted, the entire apparatus was heated to drive out any oxychloride that might be present. After this the apparatus was allowed to cool, admitting more chlorine to keep out air and then it was evacuated and sealed off. After the product had been sublimed out of the first tube, this was sealed off, and the second one placed in the furnace to sublime the product into the small tubes in which it was to be contained for storage and use. These small tubes could then be sealed off and preserved.

Vapor Density.—The apparatus used for measuring the vapor density is shown in Fig. 1. The furnace was made of a piece of copper pipe one and three-quarters inches inside diameter, ten inches long, and with a wall one-half inch thick. It was covered with asbestos paper, uniformly wound with nichrome wire, covered with alundum cement, packed with magnesia into a metal can and cemented at the openings with fire clay. Copper disks one-half inch thick served as base and cover. The lower one con-

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[3] Clausnitzer, *Ann.*, 196, 268 (1879).

[4] Evans and Ramsay, *J. Chem. Soc.*, *45*, 62 (1884).

[5] Chambrie, Bull. *soc. chim.*, *2*, 803 (1890).

[6] Beckmann, Z. *physik. Chem.*, *70*, 1 (1910).

tained an opening for the thermocouple and the upper one an opening for the capillary. Two loops of heavy copper wire formed handles for the cover A copper tube one-quarter inch inside diameter, one inch outside and about six inches long was connected to nichrome wires which could be used to lift, carry or support it. This tube fitted over the capillary of the glass bulb and was kept at a higher temperature than the furnace by means of a gas flame.

The pyrex glass bulb had a volume of about 135 cc. The depression in the bottom kept the material in the bulb to the outside and so near the source of heat.

The thermocouple was of copper–constantan. The wires were slipped into a capillary tube of hard glass which was then heated and bent. To prevent oxidation of the wires the tube was filled with dry carbon dioxide and the ends were sealed with cement.

To check the uniformity of the temperature in the furnace as well as assist in the calibration of the thermocouple, a glass bulb similar in shape and size to those used in the determinations was sealed to a capillary tube which connected to a two-atmosphere open-tube manometer. The bulb was filled with dry nitrogen and used as a constant volume gas thermometer. **A** comparison of the calibration of the thermocouple by this means with its calibration by use of fixed points showed no deviation within the precision of the measurements. This showed that the temperature within the furnace was uniform. The fixed points used were the boiling points of water and sulfur and the freezing points of tin and lead. The thermocouple was read by a potentiometer so arranged that one scale division on the instrument corresponded to less than one-tenth of a degree centigrade.

A small sample tube of selenium tetrachloride with the tip opened was placed in the bulb before the capillary was drawn, the bulb at that time being filled with dry nitrogen. After the capillary was drawn, the bulb was evacuated and sealed. The excess material was allowed to escape through the capillary by opening it when the temperature of the furnace was held constant at slightly above the subliming temperature. The capillary was sealed and the bulb removed from the furnace and weighed. Repeated determinations could be made by opening the tip of the capillary with a small flame when the temperature of the furnace was ten or more degrees above the temperature of the previous determination, and the tube again sealed by removing a small piece of the capillary. The barometric pressure and the temperature of the balance case were recorded for each determination. The volume of the bulb and the weight of the glass of bulb, tips, etc., were found at the end of the series of determinations. The results are given in Table I. The calculations were made using the perfect gas law.

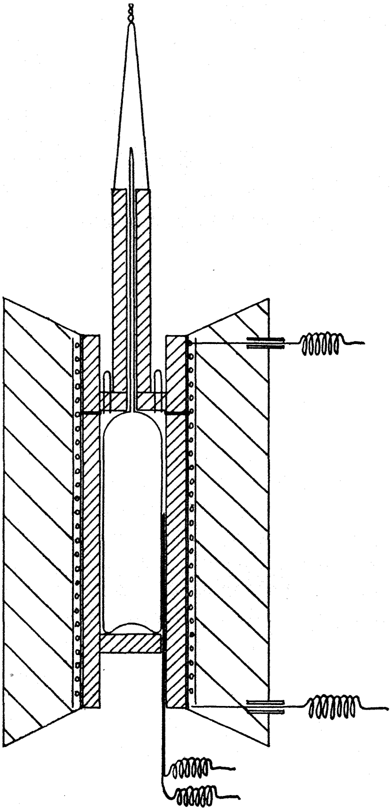
Fig. 1.—Vapor density apparatus.

The color of the bulb filled with gas just as it was taken out of the furnace varied as the temperature was raised. At the lower temperatures in the vicinity or less than 250" the gas was light yellow. As the temperature was raised, it became darker and darker until it was about the density of color of bromine vapor at atmospheric pressure. This was despite the fact that the density of the gas was decreasing as the temperature was raised. Above about 500° the shade of color seemed to remain constant.

TABLE I

VAPOR DENSITY OF SELENIUM TETRACHLORIDE

Bulb No. 1				Bulb No. 2			
Temp., °C.	Vapor density. (Hz = 2.016)	Temp., °C.	Vapor density (Hz = 2.016)	Temp., °C.	Vapor density (Ha = 2.016)	Temp., °C.	Vapor density (Hz = 2.016)
208	110.9	360.5	110.4	202.5	113.6[a]	352	111.1
225	111.2	376	110.6	215.5	111.7	368	111.4
243	110.2	406	109.9	234	111.2	391.5	111.1
260	110.5	435.5	110.0	252	111.2	420.5	110.9
278	110.3	466	110.1	270	111.6	450	110.8
295	110.4	493	110.5	286.5	111.1	479	111.2
312	110.7	521	109.9	303	111.3	508	111.0
328	110.8	574.5	109.9	320	111.6	548.5	111.1
344.5	110.4			336	111.5	600	111.2
		Av.	110.4				111.2

[a] Not averaged.

Melting and Subliming Points.—Voigt and Biltz[7] report the only attempt at determining a melting point of selenium tetrachloride. They state that between 400 and 500° the material melted in a sealed tube but a gas was evolved and the tube exploded. A thick-walled six-millimeter tube containing selenium tetrachloride was carefully sealed and placed in a furnace which had an opening so that the tube could be watched with a telescope. The temperature of the furnace was raised until the crystalline material seemed to melt; then the temperature was lowered until it crystallized again. This alternate melting and freezing was repeated a number of times. The average temperature of these determinations was 305 * 3'. The liquid formed is very dark red (almost black) and this makes it difficult to observe the formation of the crystals.

To determine the temperature at which the vapor pressure of the material is one atmosphere (the subliming point), the bulb as set up for the vapor density experiments was used. Before all the solid was allowed to escape, the capillary was sealed; then, by a careful control of the temperature of the furnace, the end of the capillary was tested with a flame to see when the glass blew out a little and when it sank in. A mean of these temperatures was taken for the value. It is 196 ± 1°.

Solubility Relations.—In order to study the solubility of selenium tetrachloride in a non-polar solvent, a small amount of the solid was placed in a tube of dry carbon tetrachloride, the tube sealed, placed in a water-bath and heated to about 100°. There was no indication of any solubility. Methyl cyanide was considered for use as a polar solvent; it, however, reacted with the crystals.

Discussion

The insolubility of this compound in non-polar solvents and apparent solubility in polar solvents[6] seems to indicate that it is polar in nature. However, due to its high melting point its solubility in non-polar solvents

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[7] Voigt and Biltz, Z. *anorg. allgem. Chem.*, 133,277 (1924).

would be small even if it were non-polar, but in that case it should be more inert to polar solvents.

The vapor density is about one-half that which the formula $SeCl_4$ would indicate. As this value remained constant for the entire temperature range of the experiments, it shows that the vapor is completely dissociated under these conditions. This confirms the results of Clausnitzer and of Chambrie but is not in agreement with those of Evans and Ramsay. This would seem to indicate a dissociation of this kind

$$SeCl_4 = SeCl_2 + Cl_2$$

However, $SeCl_2$ is not recorded in the literature. The same result for vapor density would be obtained from the reaction

$$2SeCl_4 = Se_2Cl_2 + 3Cl_2$$

as suggested by the earlier workers. There seems to be a change in the substance as heat is applied, as seen by the change in color. This is, of course, no proof but it may be an indication, for SCl_2 and $TeCl_2$ are both known, the former being red in color and the latter so dark red that it is almost black. Also SCl_2 is much deeper in color than S_2Cl_2 and so we expect $SeCl_2$ to be deeper in color than Se_2Cl_2. The author would like to suggest that the decomposition takes place to form Se_2Cl_2 at the lower temperatures (250°) and $SeCl_2$ at higher ones (500°).

As these experiments show the vapor of the material to be completely dissociated in the gas phase over the range of temperature from 200 to 600°, the mechanism of subliming must be the formation of a lower chloride and chlorine and a recombination to form the crystalline material upon cooling. The depth of color of the liquid formed by melting the crystals, as well as the very high pressure necessary, indicates a dissociation in the liquid state probably to $SeCl_2$. This may cast some doubt as to whether the molecular species $SeCl_4$ as such exists at all, for without x-ray crystal studies we do not know the molecular form in the crystal state.

Summary

A method of preparing pure selenium tetrachloride is described.

The vapor density of selenium tetrachloride has been determined from 200 to 600° at one atmosphere pressure. The vapor is completely dissociated under these conditions.

The apparent melting and subliming points of selenium tetrachloride are determined.

The solubility relations of selenium tetrachloride indicate the material to be polar in nature.

The existence of $SeCl_2$ is indicated in these experiments.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, CAMBRIDGE, ENGLAND, AND THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PROPERTIES OF TELLURIUM TETRACHLORIDE[1]

BY J. H. SIMONS

RECEIVED APRIL 14, 1930 PUBLISHED SEPTEMBER 5, 1930

In a former paper[2] the author has pointed out the fact that although the tetrahalogen compounds of sulfur, selenium and tellurium are of considerable interest in theories of molecular structure, very little is known about them.

A study of tellurium tetrachloride has added interest because of the recent investigation of Drew[3] in which he showed that $Te(CH_3)_2X_2$ went over readily to a double salt $Te(CH_3)_3X\cdot TeCH_3X_3$. This indicates that the compound has a tendency to get away from the unstable ten electron shell by two molecules associating, giving an eight electron shell to one tellurium atom and a twelve to the other. It would be interesting to see whether tellurium tetrachloride has double molecules in the gas phase.

Michaelis[4] made Victor Meyer determinations of the vapor density of tellurium tetrachloride with the following reported results.

Temp., °C.	Vapor density Experimental		Calcd. $TeCl_4$ (referred to air at same temperature)
448	9.028	9.224	9.32
530	8.859	8.464	9.32

Preparation of Tellurium Tetrachloride.—The tellurium tetrachloride was prepared in a similar manner and in an apparatus similar to that used for selenium tetrachloride.[2] As the tellurium compound distils rather than sublimes, the necks of the small reserve bulbs were restricted to facilitate sealing off. One more distillation was obtained by having an additional distilling bulb in the chain.

Melting and Boiling Points.—The melting point was obtained from the cooling curve after the material had been fused in a small electric furnace. The melting point thus determined is 225°.

The boiling point was obtained by using a glass jacketed thermocouple immersed in the vapor above the boiling liquid. The boiling point thus determined is 390° at 755.6 mm.

Solubility Relations.—Tellurium tetrachloride was found not to dissolve appreciably in carbon tetrachloride by sealing a small amount of the compound in a tube containing the dry solvent and heating in a bath of boiling water. It was found to react with solvents which would be expected to dissolve it, such as CH_3CN. No convenient solvent was found in which to determine its conductivity and freezing point lowering. Its solubility relations indicate that it is a polar compound, salt-like in nature.

Vapor Density.—The apparatus and method used to measure the vapor density of

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[1] Part of this work was done while the author was a National Research Fellow at Cambridge University.

[2] Simons, THIS JOURNAL, 52, 3483 (1930).

[3] Drew, *J. Chem. Soc.*, 560 (1929).

[4] Michaelis, *Ber.*, 20, 1780 (1887).

tellurium tetrachloride was the same as that for selenium tetrachloride. The results as shown in Table I give higher values below 500" for the apparent molecular weight than the theoretical for $TeCl_4$, and lower values at more elevated temperatures. The higher values may be due either to association of the molecules or to some difficulty in removing the material from the bulb as, for example, due to its adsorption on the walls.

TABLE I

VAPOR DENSITY OF TELLURIUM TETRACHLORIDE

Bulb No. 1				Bulb No. 2			
Temp., °C.	Vapor density (*Ha* = 2.016)	Temp., °C.	Vapor density (H_2 = 2.016)	Temp., °C.	Vapor density (H_2 = 2.016)	Temp., °C.	Vapor density (H_2 = 2.016)
420	290.3	522	269.1	429.5	297.3	528	265.6
434.5	286.9	535	267.2	441	289.9	541	261.4
450	283.1	548	263.6	457.5	284.4	554	258.9
464	280.2	561	260.2	473	276.8	568	254.9
480	277.7	573	257.3	486	276.2	581	251.8
493	273.3	587	253.6	501.5	272.9	595	246.6
507	273.2	601	250.5	515.5	268.4		

The latter explanation was suggested by the difficulty experienced in boiling out the material from the bulb at a few degrees above the boiling point. Repeated determinations gave similar results to those recorded here. As the apparatus and method functioned very well for selenium tetrachloride, it was thought that the difficulty might be due to the fact that tellurium tetrachloride is a polar liquid, and as such would be difficult to remove from the glass surface.

Above 500" the color of the vapor in the bulb became darker with higher temperature. This indicated dissociation, for $TeCl_2$ is dark red.

In order to investigate the material in the gas phase at lower temperatures to determine whether or not the molecules were associated, the following work on the vapor pressure was done.

Vapor Pressure.—The apparatus, as shown in Fig. 1, consisted of a pyrex tube containing a sealed-in bubbler joined to another tube by a ground-glass connection. The latter tube had an outlet to the air. This apparatus was placed in a furnace so that the lower end of the second tube projected below the end of the furnace. This was to allow the vapor to condense.

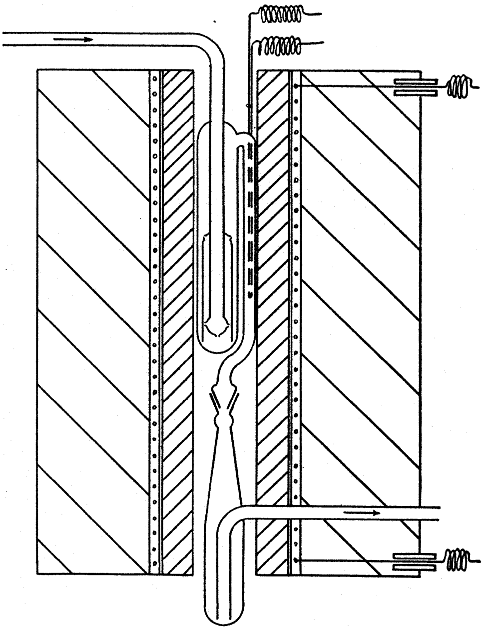


Fig. 1.—Apparatus for determining the vapor pressure of tellurium tetrachloride.

The dynamic vapor pressure method was used. A known quantity of purified and dried nitrogen was passed slowly through the apparatus while it was kept at a constant temperature in the furnace. The decrease in weight of the tube containing the tellurium tetrachloride gave the amount carried off by the nitrogen. The rate of passage of the gas was sufficiently slow to reach equilibrium with the tetrachloride, as shown by the fact that increasing or decreasing the rate had no influence on the results.

The cylinder used to measure definite volumes of nitrogen is shown in Fig. 2. Small glass points fixed in position and pointing upward provided the measuring device. A light reflected from the surface of the water showed very easily whether the point was just raising the surface of the water or was just below it. The volumes between the points could be calibrated closer than to one-hundredth of a cubic centimeter, but this was more than sufficient for our purpose. By test it was found that the eye could detect a difference in height of the water of about one three-hundredths of a millimeter, when the surface was just touching the point.

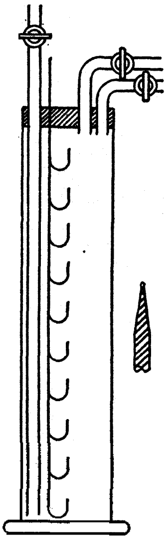


Fig. 2.—Gas measuring cylinder.

The results of these determinations are given in Table II. When the molecular weight is assumed to be the formula weight of $TeCl_4$ and the logarithms of the vapor pressure, calculated by using this assumption, are plotted against the reciprocal of the temperature, a straight line results, and this line includes the point given by the boiling point of the compound. This curve is shown in the graph. The point marked * is the boiling point. If double the formula weight is used as the assumption in the calculations, then the curve as shown by the crosses results. The true vapor pressure should give a straight line on this graph, the slope being a measure of the heat of vaporization, by the equation, $\partial \ln p/\partial(1/T) = \Delta H/R$.

TABLE II

VAPOR PRESSURE OF TELLURIUM TETRACHLORIDE

Press. N_2, mm.	Vol of N_P, cc.	Temp. of N_2, °C.	Moles of N_2	Barometric pressure, mm.	Weight of $TeCl_4$ removed from tube, g.	Temp. of $TeCl_4$, °C.	Moles of $TeCl_4$	Vapor pressure (assuming $TeCl_4$), mm.	Vapor pressure (assuming Te_2Cl_8), mm.
760.3	493.5	23.5	0.020789	759.4	0.0800	233	0.0002975	10.8	4.8
773.5	493.5	22.7	,021211	771.3	.1270	247	.000472	16.8	8.5
768.1	493.5	24 0	,020970	767.9	.1980	260	,000735	26.0	13.3
764.9	314.9	25.2	,013273	766.3	.2257	278.5	.000837	45.5	23.4
768.3	248 2	23.3	.010577	767.1	.3016	295	.001127	73.8	38.7
770.2	210.6	24.8	.008952	770.6	.4296	313	,001597	116.7	70.4
766.0	104.3	22.6	.004440	763.4	,3540	328	.001317	174.5	98.6
761.8	104.3	27 4	.004346	766.6	,3610	328	001342	181.0	102.7
765.4	47.07	26.0	.001980	767.6	,2880	345	.001070	269.5	165.3
766.0	47.07	25 0	.001988	766.7	,5738	360	,002132	396.5	268
763.2	37.60	19.8	.001610	757.4	1.7284	376	,00641	605.0	503
				Boiling point		390		755.6	

These results indicate that the molecules are not associated, or at least that there is very little association. If the molecules were double the formula weight, then the crosses should fall on a straight line. If association began below the boiling point, the line drawn on the assumption of single molecules should begin to curve at this point. This tends to prove that the high apparent molecular weight at the lower temperatures obtained in the vapor density measurements is not due to association, for if it were a very considerable association would be expected 200° lower at the temperatures of the vapor pressure measurements. This would at least be sufficient to cause a break in the vapor pressure curve, The heat of vaporization calculated from this curve is 18,400 calories per mole.

Density of Liquid.—The apparatus used in determining the density of the liquid was made of pyrex glass and is shown in Fig. **3.** The volume of the lower bulb and tube connected to it was determined by filling it with mercury to various heights and weighing it. **A fine** scratch on the glass just above the bulb was used as a reference mark from which to measure the level of the mercury. **A** telescope containing cross hairs was mounted on a traveling microscope bed for the measuring device.

Tellurium tetrachloride was run into the apparatus carefully so as not to expose it to the air. The level of the liquid in the measuring bulb was adjusted by pouring the liquid from one bulb to the other. The secondary bulb was sealed off when this was accomplished. The apparatus was then placed in a furnace which was made with copper walls one-half inch thick. It had a slit in the side so that observations could be made on the apparatus inside it. The height of the liquid in the tube was noted at different temperatures.

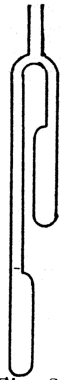


Fig. 3.—Density bulb.

The results of these determinations are given in Table III. Corrections were made both for the curvature of the meniscus and for the expansion of the glass of the bulb.

TABLE III

DENSITY OF LIQUID TELLURIUM TETRACHLORIDE

Temp., °C.	232	277	314	315	341	344	385	424	427
Density, g./cc.	2.559	2.494	2.443	2.442	2.402	2.401	2.334	2.275	2.260

Surface Tension.—A pair of capillaries which had been calibrated for surface tension measurements at room temperature were inserted in a tube which contained tellurium tetrachloride and the tube was sealed. It was then put in the above-mentioned

TABLE IV

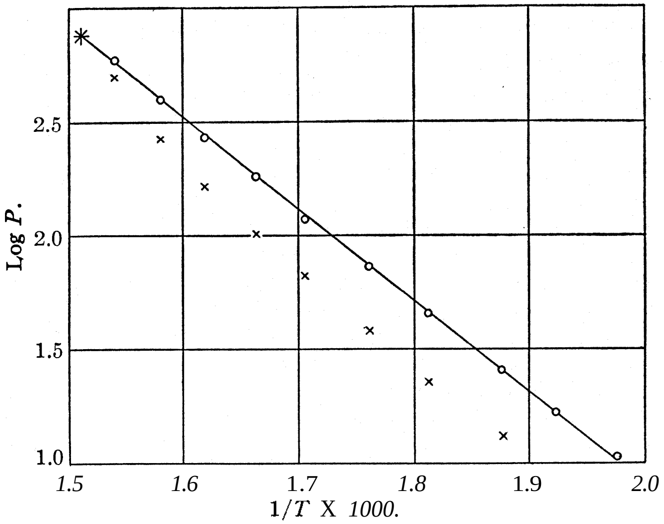
SURFACE TENSION OF TELLURIUM TETRACHLORIDE

Temp., °C.	Surface tension, dynes/cm.	Parachor	Temp., °C.	Surface tension, dynes/cm.	Parachor
238	40.2	265.8	327	33.75	267.9
260	38.3	265.7	338.5	31.85	266.0
261	38.27	265.8	352.5	31.57	267.9
263	37.70	265.1	353	31.37	267.5
280	36.87	266.2	370	30.07	267.9
298.5	35.77	267.0	397	28.37	269.3
316	34.25	267.1	413	26.93	269.1
322	34.05	267.6	413.5	26.92	269.2

furnace; after it had been kept heated for some time to make sure that the glass was wetted, the measurements were made. These covered a considerable temperature range. A close examination gave no indication of a finite angle of contact between liquid and glass. These results are given in Table IV. Corrections were made for the expansion of the glass and for the curvature of the meniscus.

The parachors[5] were calculated from thrse surface tension measurements. They are given in Table IV. The density of the vapor was calculated from the vapor pressure.

In all this work the same thermocouple was used as in the work on selenium tetrachloride.



Pig. 4.—Vapor pressure of $TeCl_4$.

Discussion

These experiments show that tellurium tetrachloride exists as $TeCl_4$ in the gas phase. Three ways of explaining its structure are the ionic form $TeCl_3^+Cl^-$, the structure containing two single electron bonds as recommended by Sugden,[6] and a form in which a ten electron shell is assigned to the central atom, four pairs of these being shared by chlorine atoms. It is difficult to understand how the first form could exist in the gas phase as a normal gas. The second form involves the assumption of single electron bonds, which is an extremely questionable hypothesis. The third form gives a structure which agrees well with the properties of the compound.

Of the tetrahalogen compounds of this family of elements tellurium tetrachloride is the only one that lends itself readily for study. The only others that are stable enough to exist in anything but a crystalline form are the fluorides and these are difficult to handle due to their reactivity with glass. The properties of tellurium tetrachloride are, therefore, to be

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[5] See Sugden, *J. Chem. Soc.*, 125, 1177 (1924).

[6] Sugden, *ibid.*, 1058 (1929).

considered as representing the general properties of ten electron shell compounds in which one electron pair of the central atom is not shared.

Summary

A method for the preparation of pure tellurium tetrachloride is described.

The melting point and boiling point of tellurium tetrachloride are determined to be 225 and 390°, respectively.

The vapor density of tellurium tetrachloride is measured from above the boiling point to 600°.

The vapor pressure of liquid tellurium tetrachloride is measured.

The heat of vaporization is determined to be 18,400 calories per mole.

The vapor of the compound is concluded to consist of single molecules of $TeCl_4$ from the melting point to about 500°, where dissociation begins.

The density of liquid tellurium tetrachloride is determined from the freezing point to above the boiling point.

The surface tension of tellurium tetrachloride is determined over the same range.

Tellurium tetrachloride is concluded to have a ten electron shell surrounding the central atom, four pairs of these being shared with the chlorine atoms.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE PEARSON CHEMICAL LABORATORY OF TUFTS COLLEGE]

THE STANDARDIZATION OF A MODIFIED OSTWALD VISCOMETER

BY H. M. CHADWELL AND B. ASNES

RECEIVED APRIL 18, 1930 PUBLISHED SEPTEMBER 5, 1930

A viscometer conforming essentially to Washburn and Williams,[1] modification of Ostwald's viscometer has been used by one of us[2] to determine the viscosities of several aqueous solutions, without attempting to determine how accurately the instrument reproduced true viscosities. The viscosities were calculated both by the simple law of Poiseuille and by assuming a value of 1.12 for m, the coefficient of the correction term which has been variously called the kinetic energy, Hagenbach, or inertia correction. Washburn and Williams reported experiments on changing time of flow with changing pressure, to support the conclusion that the law of Poiseuille, without a correction, should be used, but their method of calculation has since been questioned.[3] Since the magnitude of m is thought to be dependent upon the shape of the terminal of the capillary as well as

[1] Washburn and Williams, THIS JOURNAL, 35, 739 (1913).

[2] Chadwell, *ibid.*, 48, 1912 (1926).

[3] Dorsey, J. Opt. *Soc. Am.*, **14**, 45 (1927).

upon the velocity of flow,[3] the present investigation was undertaken to determine how nearly an instrument of this type reproduced absolute viscosities.

At least two methods of standardizing a viscometer are available. The method usually adopted is to vary the time of flow of a standard substance by varying the pressure by known amounts. The necessary apparatus is complicated.[4] The second method is based on the measurement of times of flow for liquids of known viscosity. Of the data for the various liquids recommended as reference materials, those for water are the most trustworthy. A variation in time can be obtained by varying the temperature.

This paper reports the use of three viscometers, similar to one another in size of capillary and general construction, but differing in the shape of the ends of the capillary tube, ranging from a decided trumpet to the square end of a fractured tube. The dimensions of these viscometers were measured carefully, and the time of flow of water was measured at seven temperatures ranging from 15 to 30°. The resulting data are compared with the viscosity of water as given by previous investigations. The viscosities of aqueous solutions of urethan, determined at 20 and 25°, are given to provide standard solutions to be used as reference materials for future calibration.

Apparatus and Results for Water.—The three viscometers were all of the same type and constructed of pyrex glass, similar to that used before by one of us.[2]

Viscometer I had its capillary sealed into the instrument in such a way that its ends were decidedly trumpet shaped. The capillaries of Viscometer II and III were taken from the same piece of tubing. The capillary in Viscometer II was not sealed into the instrument, but connected by ground joints, sealed on the outside with de Khotinsky cement. Its ends were the square fractures obtained by breaking the tubing. Viscometer III had its capillary sealed in, but with more abrupt endings than Viscometer I, instructions being given to the glass-blower to make the endings as abrupt as possible. The inside diameter of the tubes into which the capillaries delivered the liquid was 8 mm.

Each viscometer was mounted on a brass frame in such a way that the capillary was held in a vertical position in the thermostat. Each frame had three brass reference points that fitted into corresponding small conical cups inside the thermostat.

The thermostat was made from a deep glass jar, insulated as usual, and was fitted with a copper cooling coil, a stirrer and an automatic electrical heating unit. The temperature remained constant to within ±0.002° at all temperatures except 15°, where the variation was slightly larger. Into the jar was built a superstructure of brass to hold the frame of the viscometer in a rigid and definite position. It was found convenient to construct a frame outside of the thermostat with the reference points in similar positions to facilitate the measuring of the dimensions of the instruments. Windows through the packing of plumber's wool were provided so that the movements of the liquid past the scratches could be viewed easily.

The temperatures which the thermostat maintained were obtained with a series of

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[4] Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, 1922.

Beckmann thermometers that were used as secondary standards, each one being compared with a platinum thermometer. The platinum thermometer had been calibrated by the Bureau of Standards and has been described in THIS JOURNAL.[5] Each comparison with the platinum thermometer was made within 0 01° of the desired temperature, so that any corrections to the Beckmann were eliminated It is believed that these temperatures were accurately reproduced within a few thousandths of a degree.

The diameters of the capillary tubes were determined by measuring the length of a small drop of mercury at a known temperature. The mercury was later weighed on an assay balance with weights that had been compared with weights certified by the Bureau of Standards. The measurements of length were made with a "Universal Reading Microscope," manufactured by P W G Pye & Co. The screw with micrometer head read to 0.005 mm. The larger scale, 18 cm long, could be read with a vernier to 0.05 mm.

In the determination of the radius of the capillaries the mercury used had been purified by washings with nitric acid followed by distillation. The readings of the length of the thread of mercury were made at points equally distributed along the capillary. The results of these measurements are given in Table I.

TABLE I

MEASUREMENTS DETERMINING THE RADIUS OF THE CAPILLARIES

Corrected weight of mercury	No of settings	Mean length, cm.	Density of mercury	Radius. cm
		Viscometer I		
0 05593	3	2 2695	13.539	0.024068
,06617	4	2 6814	13 539	.024087
.06253	6	2 5311	13.541	.024099
			Mean	,024085
		Viscometer II		
0 30874	1	13 380	13.537	0.023293
.27087	1	11 765	13 543	.023262
.28076	1	12 170	13.538	.023290
,09614[a]	3	4 150	13 540	.023337
.28042	1	12 155	13 540	.023289
.06282	6	2.7248	13.538	.023283
			Mean	.023283
		Viscometer III		
0.20906	3	9.117	13 524	0.023232
.28815	2	12.565	13.520	,023236
,35810	1	15 600	13 533	.023236
			Mean	.023234

[a] Omitted in the calculation of the mean because of evident irregularity.

In the values of the "mean length" and the "radius," the last decimal place is significant only in determining the next figure. The "No. of settings" refers to the number of measurements of the length of each drop of mercury as it appeared at different positions in the capillary.

In calculating the radius of each capillary from the weight of mercury and the length of the drop, a correction was applied for the meniscus.

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[5] Chadwell, THIS JOURNAL, 49,2795 (1927).

This correction was calculated by measuring the height of the meniscus with a microscope having a magnification of 100 and fitted with a micrometer eyepiece. The latter was calibrated by a Bausch and Lomb test plate graduated in 0.01 mm. It was assumed that the meniscus was a spherical segment.

The values of the radius given above are calculated on the assumption that the bore is cylindrical. Formulas[6] have been advanced for capillaries which do not conform with this condition. If the capillary is elliptical

$$\frac{2B^3C^3}{B^2 + C^2} \tag{1}$$

is substituted for R^4 in the formula for viscosity, where B and C are the major and minor semi-axes of the cross section. If the capillary is a frustum of a circular cone, R^4 is replaced by

$$\frac{3R_1{}^3R_2{}^3}{R_1{}^2 + R_1R_2 + R_2{}^2} \tag{2}$$

where R_1 and R_2 are the radii at the two ends. If the capillary is a frustum of an elliptical cone, R^4 is replaced by

$$\frac{3R_3{}^3R_4{}^3}{R_3{}^2 + R_3R_4 + R_4{}^2} \times \frac{(1 - E^2)^3}{1 + E^2} \tag{3}$$

where R_3 and R_4 are arithmetical means of the major and minor axes at their respective ends, and $E = (B - C)/(B + C)$. B and C have the same meaning as in (1).

To determine how great an assumption was introduced in using the simplest method of calculating the radius, the individually determined radii of Viscometer I were plotted against the position of the drop of mercury and the curve extrapolated to give the radii at the ends. The results were 0.02430 and 0.02388. If these data are substituted in expression (2), the corrected value for R^4 comes out equal to 0.0633669, while that used in the calculations was 0.0633650, a difference of 0.06%.

A short section of the capillary used in Viscometers II and III was examined under a microscope fitted with a micrometer eyepiece and previously calibrated with a Bausch and Lomb test plate. This showed the cross section to be circular within the accuracy of the examination (between 1 and 2%). If there was a difference in the semi-axis of 2%, the difference in the value of R^4 would be only 0.04%. As a consequence of these measurements, it was felt that the first values for the radius could be used with safety.

The other dimensions of the instruments were determined in the usual way, with corresponding accuracy. They are summarized in Table II.

In the determination of the time of flow of water the usual precautions were taken in regard to cleanliness and absence of dust. The water was

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[6] See Bingham, **Ref. 4, p.** 69.

TABLE II

SUMMARY OF DIMENSIONS OF VISCOMETERS

	Vis. I	Vis. II	Vis III
Radius of capillary, cm..	0.024085	0.023283	0.023234
Length of capillary, cm.. . .	17.25	17.225	16.540
Volume of upper bulb, ml.	7.150	5.336	8.874
Volume used in viscometer, ml.. .	68.53	50.54	60.88
Distance between scratches, cm..	6.065	5.960	5.744
Difference in water levels at start, cm.	24.148	22.285	22.966
Difference in water levels at end, cm.	17.910	16.270	17.010
Mean head *(h)* by Meissner (Eq. 6)	20.880	19.120	19.841

thrice distilled, from alkaline permanganate and dilute sulfuric acid, using tin condensers. The time of flow was measured, as in the former investigation,[7] by a stop watch having an excellent Swiss movement and recording time to one-fifth of a second. It was verified frequently and kept in a constant state as regards winding and position.

The times of flow for water for the different temperatures, as recorded in Table III, are average results of at least three runs in which the variation was not greater than the accuracy of measuring the time of flow (1/5 sec.). Table III also includes the data for the density of water in air and the viscosity, expressed as poises, as given by the Bureau of Standards[8] and the "International Critical Tables."[9] These data are used in subsequent calculations.

TABLE III

DATA POR WATER

Temp., °C.	Time of flow Vis. I	Vis II	Vis III	Density in air	Viscosity B. of S.	I. C. T.
15.00	523.2	493 3	765.6	0.99790	0.011404	0 011447
18.00	484.4	457.9	709.0	.99741	,010559	,010603
20.00	461.3	436.3	674.7	.99703	.010050	,010087
22.00	439.8	415.6	643.5	.99660	.009579	.009608
25.00	410.6	388.6	600.8	.99589	.008937	.008949
27.00	392.8	371.2	574.5	.99536	.008545	.008551
30.00	368.6	348.5	539.1	.99451	.008007	.008004

Calculation of Results

The viscosity is related[10] to the dimensions of the viscometer by the formula

$$\eta = \frac{\pi r^4 p t}{8V(l + e)} - \frac{m\rho V}{8\pi(l + e)t} \tag{4}$$

where η is the coefficient of viscosity (in poises), r the radius (cm.) of the capillary assumed to be cylindrical, p the over-all driving pressure, t the

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[7] Chadwell, Ref. 2, p. 1916.

[8] Bingham and Jackson, "Bull. U. S. Bureau of Standards," 14, No. 298 (1917).

[9] "International Critical Tables," McGraw–Hill Book Co., Inc., 1929, Vol. V, p. 10.

[10] See, for instance, Dorsey, Phys. *Rev.*, 28, 833 (1926).

time of flow in seconds for a volume of V (ml.) through a tube of length l cm., e the Couette correction, m a numerical factor usually taken as 1.12, and p the density of the liquid.

It follows from this formula that if $\eta/\rho t$ is plotted as ordinates and $1/t^2$ as abscissas for liquids of different known viscosity, the slope of the line to the axis of abscissa is

$$tan\,\Theta = -\frac{mV}{8L\pi}$$

where Θ is the angle between the line and the axis and L is the effective length ($L = l + e$). The intercept on the axis of abscissa is π^2r^4hg/mv^2 and the intercept on the axis of ordinates is $\pi r^4hg/8$ VL where "h" is the effective height causing the liquid to flow by its own hydrostatic pressure ($p = h\rho g$) and g is the force of gravity. If m is zero, the line will be parallel to the axis of ordinates.

It should be emphasized, in support of this method, that one can conclude whether m has a value other than zero quite independently of any measurements of the dimensions of the capillary. If it is zero, the conclusion depends upon the values of viscosity taken as standard, the density of the liquid and the time of flow; if m does not equal zero, its value is calculated from measurements of the volume of the liquid and length of capillary, not upon the radius.

This method of evaluating m is not new. It is similar to the method of Knibbs[11] where one liquid is used to calibrate a viscometer by allowing it to flow under different pressures, and then plotting pt against $1/t$. Nor is it very dissimilar from that of Herschel,[12] who uses a series of liquids of known viscosity and plots Reynolds' criterion ($R = vd\rho/\eta$ where v, the velocity, is equal to $V/\pi r^2t$, and d is the diameter) against η'/η, the ratio of the viscosity as calculated without the second term of Formula 4 and using the measured length (l), to the true viscosity (η). By this method the intercept on the axis of η'/η is equal to $(1 + e)/l$ and the slope of the line gives the value of m by the formula $m = 32\,l/d\cdot\tan 8$.

Both the method suggested by the authors and Herschel's method of evaluating m presuppose the knowledge of certain viscosities, either of one liquid at different temperatures or different liquids at the same temperature. Since water has been studied more carefully than any other liquid, it was selected as the basis of comparison, and used at different temperatures as described above.

The data for the absolute viscosity of water as determined by various investigators have been recalculated by Bingham, assuming that m has

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[11] See *Rieman*, THIS *JOURNAL*, *50*, 46 (1928). *Since* this *manuscript was prepared it has* been found *that* Higgins *has* used the same *method* of *plotting* $\eta/\rho t$ *against* $1/t^2$. *Higgins, J. Soc.* **Chem. *Ind.*,** **32,** 568 (1913).

[12] *Herschel,* ***Proc. Am.*** *Soc. Test. Mat.*, 19, 677 (1919); *also Herschel and Bulkley,* ***Ind. Eng.*** *Chem.*, 19, 134 (1927).

a value of *1.12.* They have been published in several places.[13] When made the basis for evaluating m for Viscometer I by the first method suggested, the values for $\eta/\rho t$ as given in Table IV result.

TABLE IV

VALUES OF $\eta/\rho t \times 10^5$ FOR VISCOMETER I BASED ON THE ABSOLUTE VISCOSITY OF WATER AS DETERMINED BY VARIOUS INVESTIGATORS

Temp,	Poiseuille					Thorpe and	Bingham and
°C.	A	C	D′	E	Sprung	Rodger	White
15	2.1807	2.1958	2.1960	2.1942	2.1709	2.1690	2.1784
20	2.1803	2.1901	2.1879	2.1931	2.1694	2.1753	2.1860
25	2.1765	2.1921	2.1926	2.1943	2.1880	2.1766	2.1863
30	2.1708	2.2063	2.2049	2.2093	2.2519	2.1727	2.1798

The columns under "Poiseuille" contain his results for four different capillaries. If m for our viscometers had a value of zero, the term $\eta/\rho t$ should be independent of the time of flow; if m had a positive value, $\eta/\rho t$ would have to decrease with a decrease in time (increase in temperature). It is evident from the data of this table that any conclusion concerning m would be uncertain.

The determinations of the absolute viscosity of water have been critically appraised by two reviewers[8] The Bureau of Standards has accepted the formula

$$t = A(\varphi + D) + C - \frac{B}{\varphi + D} \tag{5}$$

to define the changes in fluidity with temperature, where t is the centigrade temperature, φ the fluidity and A, B, C and D are arbitrary constants having the values *0.23275,* 8676.8, *8.435* and *1.20,* respectively. The second set of data were compiled by the editors of the "International Critical Tables."[9] No information is available concerning the basis of their selection. Both sets of values have been included in Table III. They are the basis for calculating the values of $\eta/\rho t$ given in Table V.

The values of $\eta/\rho t$ are remarkably consistent for the Bureau of Standards data. Viscometer II, having fractured ends, is slightly less regular (the value for 15° is evidently in error) but shows no tendencies that can be attributed to the configuration of the terminals of the capillary. *It is to be concluded that viscosities corresponding to the Bureau of Standards data (Bingham and Jackson) could be reproduced by any of the viscometers at the velocities studied, on the assumption that m equals zero, in other words, by calculating the results by the simple Poiseuille formula.*

The values of $\eta/\rho t$ calculated from the "International Critical Tables" data show a decided trend. From them a value of m for each viscometer can be calculated. The data for 15° are so discordant that they are mean-

[13] Bingham and Jackson, *Sci.* Paper Bur. *Stand.,* No. 298 (1917); Landolt–Börnstein, "Physikalisch-Chemische Tabellen," Erster Ergänzungband, 1927, p. 83; Bingham, **Ref.** 4, p. 339.

TABLE V

VALUES OF $\eta/\rho t$ FOR THE THREE VISCOMETERS USING η_{H_2O} ACCORDING TO THE BUREAU OF STANDARDS

	$\eta/\rho t \times 10^5$			% Deviation from average		
Temp., °C.	Vis. I	Vis. II	Vis. III	Vis. I	Vis. II	Vis. III
15.00	2.1843	2.3166[a]	1.4926	−0.04	+0.23[a]	−0.06
18.00	2.1854	2.3119	1.4931	+ .01	− .03	− .03
20.00	2.1851	2.3103	1.4939	± .00	− .04	+ .03
22.00	2.1855	2.3127	1.4937	+ .02	+ .06	+ .01
25.00	2.1856	2.3093	1.4937	+ .02	− .08	+ .01
27.00	2.1856	2.3128	1.4943	+ .02	+ .06	+ .05
30.00	2.1842	2.3103	1.4934	− .04	− .04	± .00
Average	2.1851	2.3112	1.4935	.02	.05	.03

[a] Not included in average.

VALUES OF $\eta/\rho t$ FOR THE THREE VISCOMETERS USING η_{H_2O} ACCORDING TO "INTERNATIONAL CRITICAL TABLES"

	$\eta/\rho t \times 10^5$			% Deviation from average		
Temp., °C.	Vis. I	Vis. II	Vis. III	Vis. I	Vis. II	Vis. III
15.00	2.1925	2.3254	1.4982	+0.10	+0.34	+0.08
18.00	2.1946	2.3215	1.4993	+ .20	+ .17	+ .15
20.00	2.1931	2.3208	1.4994	+ .13	+ .14	+ .16
22.00	2.1921	2.3196	1.4982	+ .09	+ .09	+ .08
25.00	2.1885	2.3124	1.4957	− .08	− .22	− .09
27.00	2.1871	2.3142	1.4953	− .14	− .14	− .11
30.00	2.1834	2.3094	1.4928	− .31	− .35	− .28
Average	2.1902	2.3176	1.4970			

ingless, and so are not included. For Viscometers I and III, having the capillaries sealed into the glass and as a consequence having trumpet-shaped openings, the values can be determined graphically (by the method outlined above). Figure 1 shows the plot of $\eta/\rho t$ against $1/t^2$. The slopes of the lines are -0.0355 and -0.0487, leading to values of m of 2.15 and 2.27. The data for Viscometer II (having squarely cut ends) are not close enough to a straight line to insure much confidence in the result. The slope of the most probable straight line was calculated by the method of least squares as -0.0364, which corresponds to values of m equal to 2.93. It would seem that the data from the Bureau of Standards, with the accompanying conclusions, are the most trustworthy.

When Herschel's method is applied to these data, the conclusions regarding m are, of course, the same, but it also produces the Couette correction. This method has been applied to the data for the three viscometers, using the viscosity of water according to the Bureau of Standards. The results are given in Table VI, where R represents Reynolds' criterion. In order for m to have a value other than zero, the data for η'/η would have to show a definite trend, for m is a function of the slope of the line when R is plotted against η'/η.

According to this method the Couette correction (e) is given by the

TABLE VI

HERSCHEL'S METHOD APPLIED TO THE THREE VISCOMETERS USING η_{H_2O} ACCORDING TO THE BUREAU OF STANDARDS

	Viscometer I		Viscometer II		Viscometer III	
Temp., °C.	R	η'/η	R	η'/η	R	η'/η
15.00	31.61	1.0041	25.88	1.0160[a]	27.79	1.0161
18.00	36.85	1.0036	30.10	1.0180	32.40	1.0157
20.00	40.64	1.0038	33.18	1.0187	35.75	1.0152
22.00	44.71	1.0036	36.52	1.0177	39.31	1.0153
25.00	51.29	1.0035	41.84	1.0192	45.10	1.0153
27.00	56.04	1.0035	45.78	1.0177	49.30	1.0149
30.00	63.68	1.0041	51.99	1.0187	56.02	1.0155
Average		1.0037		1.0183		1.0154

[a] Not included in the average.

expression $e = l(a - 1)$ where a is the intercept on the η'/η axis corresponding to $R = 0$. The calculated corrections are 0.064, 0.315 and 0.255 cm. for the three viscometers. It is not to be expected that these values of the Couette correction would bear the relationship to the radius as derived from theoretical considerations. They really represent a correction to one particular measured dimension of the capillary to counteract inaccuracies in the others. The real Couette correction for these viscometers is almost negligible, for the ratio of l/r is so large, the correction being much smaller than the uncertainty in measuring the length of a capillary terminating in trumpet-like openings.

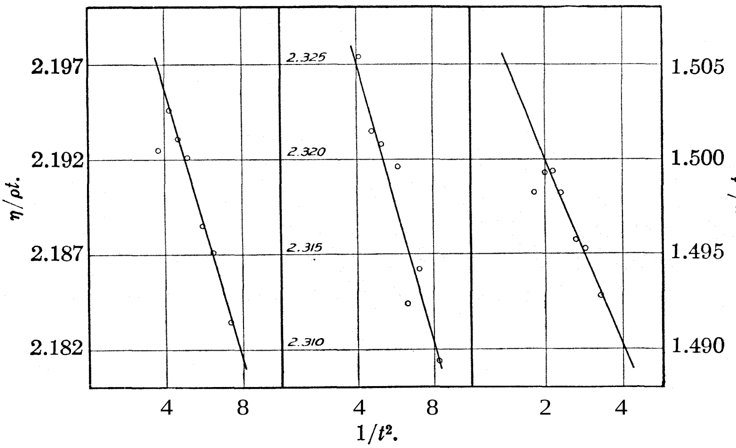

Fig. 1.—The values of η/pt ($\times 10^5$), using the data of "International Critical Tables" for the viscosity of water, are plotted against $1/t^2$ ($\times 10^6$) for the three viscometers. The slopes of the lines give the values of m.

These results are of interest in relation to Dorsey's[14] interpretation of

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[14] Dorsey, *Phys. Rev.*, 28, 833 (1926); and *J. Opt. Soc. Am.*, 14, 45 (1927).

Poiseuille's and Bond's[15] experiments on the flow of liquids through capillaries. Dorsey maintains that the data show that when Reynolds' number (R) is less than 10, m has a value of zero and the Couette correction (e) is 1.146 r. If R is greater than 10, two regimes are possible if the capillary is long and free from mechanical vibration. In the one case m still remains equal to zero; in the other, and the more likely, m is probably equal to unity and e is half as large as before. A theoretical interpretation of the stability of these regimes is given, based on the premises "that the free surface of the liquid in each reservoir is great compared with the sectional area of the capillary, that the edge at each terminus of the capillary is sharp and smooth, that at each end of the capillary the terminal face is normal to the axis of the capillary, and that the radial extent of this face, in every direction, and all other distances from the terminus to the wall of the reservoir are severally so great that the distribution of the flow of the liquid is essentially the same as if they were infinite." It is further pointed out that departures from these ideal conditions will result in different values of m and e, and probably account for the variations actually found in determined values of m between 1.0 and 2, and averaging 1.12. Variation in the configurations of the terminals of the capillaries are probably the most significant.

The velocities of flow through the three viscometers studied were sufficiently large to allow either of the two regimes to be satisfied, for the values of Reynolds' number were between 25 and 65. Furthermore, Viscometer II had a capillary with terminals which fulfilled the postulated conditions, particularly that of a sharp-edged face normal to the axis of the capillary, while the others had terminals that were trumpet-like, Viscometer III having a more abrupt opening than Viscometer I. Yet there is little or no evidence in the data given above to show that the configuration of the capillary ends in these particular viscometers played a part in determining m.

Equation 4 has been used in various ways to evaluate different dimensions of the viscometer. Reference has already been made to Knibbs' method, which produces the value of m and r, and to Herschel's method yielding m and e. Dryden's equation[16] for the evaluation of the hydrostatic head causing the flow is still another modification, but these methods can hardly be used simultaneously.[17] The value to be used for the over-all driving pressure (p) is particularly hard to evaluate for a viscometer of the Ostwald type, for the hydrostatic head is varying during the flow of liquid. The average head is certainly in error.[18] The chronological average head

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[15] Bond, *Proc. Phys. Soc. London*, 33, 225 (1921); *ibid.*, 34, 139 (1922).

[16] Reported in a paper by Herschel, Bureau of Standards Tech. Paper, No. 210, 230 (1922).

[17] See Herschel and Bulkley, *Ind. Eng. Chem.*, 19, 134 (1927).

[18] See Lidstone, *Phil. Mag.*, [VI] 43, 354 (1922).

has sometimes been evaluated by an integration method applied to observed changes of head at intervals of time throughout the flow. This pressure is more generally calculated from the approximation formula of Meissner

$$h = \frac{h_1 - h_2}{\log^* h_1/h_2} \qquad (6)$$

where h_1 is the initial and h_2 the final hydrostatic head. This latter method when applied to our viscometers produced the values listed under the heading "h" in Table II. To determine how different these values of effective heads are, the correct value to be used to give the mean value of $\eta/\rho t$ in Table IV was calculated from $h = \frac{8VL}{\pi r^4 g}\left(\frac{\eta}{\rho t}\right)_{\text{mean}}$ assuming the Couette correction to be that given by Dorsey. The results are summarized in Table VII.

TABLE VII

HYDROSTATIC HEADS CALCULATED BY VARIOUS METHODS

No. of viscometer	h_a	h_m	h_η
I	21.029	20.880	20.838
II	19.278	19.120	18.805
III	19.988	19.841	19.571

Here the arithmetic average of the initial and final heads'is given as h_a, the values by Meissner's formulas as h, and the values calculated from the viscosity as h_η. The percentage differences between the last two columns are 0.2, 1.6 and 1.4, respectively, for the three viscometers.

The above comparison should not be interpreted to measure the approximation of Meissner's formula, for all of the inaccuracies in measurements of the dimensions of the capillaries are automatically included. It is rather disconcerting, however, that the capillary for Viscometer II, which was the easiest to measure, shows the largest deviation. Furthermore, it should be remembered that Meissner's formula was derived on the assumption that the two limbs of the viscometer are cylindrical and equal, and these conditions are not satisfied in the design of the viscometers in question.

For an exact determination of m, the length of the capillary tube should be relatively small so that the kinetic energy correction is large. This procedure was followed by Rieman,[19] who concluded that the value of m was 1.12. A Bingham viscometer was used, modified to the extent that the capillary was mounted in rubber tubing and had, presumably, squarely fractured ends. The times of flow under varying pressure were determined and the value of m calculated by the method of Knibbs. The velocities of flow were very different from those reported in the present investigation, Reynolds' number varying from 192 to 1013.

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[19] Rieman, THIS JOURNAL, 50, 46 (1928).

In the standardization here reported, the primary objects were to determine how exactly a viscometer essentially of the Washburn and Williams type reproduced absolute viscosities, and to determine the effect of different configurations in the terminals of the capillary. We believe that the investigation has shown that these viscometers would reproduce viscosities comparable to the values of water accepted by the Bureau of Standards (Bingham and Jackson), and at the velocities used, on the assumption that *m* equals zero. If further investigation changes the absolute viscosities of water, the data determined by these viscometers must be changed. We would emphasize the need of evaluating *m* for a given viscometer, and for a given range of velocities of flow. We do not wish that our conclusions be interpreted to mean that the kinetic energy correction can be neglected in determining viscosity.

The Viscosity of Aqueous Solutions of **Urethan.**—In order to have liquids available for standardization of other viscometers, the viscosities of several aqueous solutions of urethan were determined with Viscometer I.

Urethan was selected primarily because of its ease of purification by recrystallization. Other substances have been recommended for standardizing purposes, particularly aqueous solutions of alcohol and of sucrose. The latter was discarded from consideration because of the difficulty of purification and because the solutions were liable to mold. Alcohol is a difficult substance to free from aldehyde and water. At the beginning of this investigation it was thought that alcohol–water mixtures could be used as well as water in the preliminary standardization, but the results in the literature were more discordant than those of water, and several weeks spent in purifying alcohol led to the conclusion that although relatively pure alcohol could be prepared, the sample obtained would not be comparable to those of previous investigators and certainly could not be easily reproduced in the future.

Purification of Materials

Urethan.—Urethan ($NH_2COOC_2H_5$) from a reliable source was crystallized four times from water, the crystals being separated from the mother liquor by a centrifuge. The material was dried and kept in a desiccator over solid sodium hydroxide until the solutions were prepared.

The melting points were determined by immersing a standardized tenth degree thermometer in a mush of the melted urethan, surrounded by an air jacket and immersed in a bath of warm sulfuric acid. The thermometer reading was corrected for emergent stem, zero point and scale deviation. The melting point of the material after four crystallizations was the same as after three, namely, 48.19°. This is slightly higher than the values obtained previously of 47.94 and 47.99°.[20]

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[20] Richards and Chadwell, THIS JOURNAL, **47**, 2283 (1925). For other values for the melting point, see Ref. 7 in that paper.

Water.—The water was triply distilled as usual and was purified directly before the solutions were prepared.

Preparation of **Solutions** and Measurement of Viscosity.—The solutions were prepared in 100-cc. graduated flasks, their concentrations being determined by weighing to milligrams on an analytical balance. Precautions were taken to prevent evaporation by adding the water last, and by keeping the bottles sealed with collodion. In a few cases the solution contained small particles of lint, in which event it was filtered rapidly into another flask. Vacuum corrections were not applied for they would have changed the percentage by only 0.01%.

The densities were determined in duplicate in 10-cc, Ostwald pycnometers, weighing against a sealed counterpoise,[21] and corrected to the vacuum standard.

The technique of making a viscosity measurement was the same as with water. All of the runs were made with Viscometer I, the determinations at 25° being completed before the thermostat was changed to 20°. Frequent runs were made with water to ascertain that the apparatus was functioning properly. The time for each solution was the mean of at least two runs, concordant within the accuracy of measuring time.

In Table VIII are given the results of these experiments. In the first column is given a letter to represent the order of runs, in the second the percentage of urethan by weight and in the third the number of moles of urethan (mol. wt., 89.062) per 1000 g. of solution. The values for density are corrected to the vacuum standard. When used in calculating the viscosity they are changed to the density in air by subtracting the weight of 1 ml. of air. The viscosities are expressed as centipoises (the viscosity in poises $\times$ 100) and were calculated by the formula $\eta = 2.1851\, pt \times 10^{-5}$ based on the results given in Table V. In other words, the viscosities given above are referred to the viscosity of water as given by the Bureau of Standards.[22]

Table IX includes the viscosities (in centipoises) and fluidities (in reciprocal poises) for these urethan solutions obtained by interpolation from the curve of the ratio of change in viscosity to molarity plotted against molarity (η solution $- \eta H_2O/c$ vs. c). The data in Table VIII are consistent with the exception of Solution E, whose viscosities at both temperatures are slightly high.

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[21] Richards and Chadwell, THIS JOURNAL, 47, 2286 (1925).

[22] These results at 20° are in good agreement with those determined by Richards and Palitzsch [*ibid.*, 41, 63 (1919)]. Their values for the relative viscosity, which they calculated by the simple Poiseuille formula, are as follows

%	9.12	16.69	28.62	44.51	50.07	55.65
η	1.206	1.398	1.730	2.250	2.471	2.716

By interpolation of our results we get for viscosities at the three lowest concentrations the following: 1.206, 1.402 and 1.730. Our density values are slightly lower than those of Richards and Palitzsch.

TABLE VIII

THE VISCOSITY OF URETHAN SOLUTIONS

No.	%	c	20° t	20° $\rho_{\text{vac.}}$	20° η(cp.)	25° t	25° $\rho_{\text{vac.}}$	25° η(cp.)
	0	0	461.3	0.9982	1.005_0	410.6	0.9971	0.893_5
D	5.270	0.591_7	511.4	1.0049	1.121_6	453.0	1.0033	0.991_9
A	10.812	1.213_9	567.6	1.0115	1.253_0	500.3	1.0097	1.102_5
E	14.869	1.669_5	611.4	1.0164	1.356_3	538.2	1.0143	1.191_4
B	20.549	2.307_3	674.1	1.0229	1.504_9	589.8	1.0205	1.313_6
F	24.599	2.762_0	721.7	1.0273	1.618_2	629.9	1.0247	1.408_7
C	28.815	3.235_4	774.2	1.0316	1.743_1	673.5	1.0290	1.512_6
G	41.464	4.655_6	946.7	1.0437	2.156_5	819.4	1.0403	1.860_5

TABLE IX

VISCOSITIES AND FLUIDITIES OF URETHAN SOLUTIONS (FROM SMOOTH CURVES)

c	20° η(cp.)	20° φ	25° η(cp.)	25° φ
0.0	1.005_0	99.50	0.8935	111.92
.5	1.1032	90.65	$.976_4$	102.42
1.0	1.2067	82.87	1.0636	94.02
1.5	1.3157	76.01	1.1553	86.56
2.0	1.4310	69.88	1.2517	79.89
2.5	1.5525	64.41	1.3533	73.90
3.0	1.6806	59.50	1.4605	68.47
3.5	1.815_6	55.08	1.573_6	63.55
4.0	1.9582	51.07	1.6931	59.06
4.5	2.1075	47.45	1.8201	54.94

It might be argued that it was unsafe to assume that the viscometer would reproduce viscosities over a greater range than was used in the standardization, that m might change from its value of zero. If we base a conclusion on Dorsey's analysis, this might very well be the case for greater velocities of flow, but quite improbable for smaller. As a consequence, confidence is felt that these solutions can be used for future standardizations. It would be interesting to see what the viscosities of these solutions would be if determined with an instrument with which it had been demonstrated that m had a value different than zero, and which reproduced the Bureau of Standards data for water.

We are indebted to the Elizabeth Thompson Science Fund for providing a grant to aid this investigation.

Summary

Three viscometers of the Ostwald type as modified by Washburn and Williams have been constructed similar to each other with the exception of the configuration of the ends of the capillaries, which varied from gradual trumpets to squarely fractured ends. The dimensions of these viscometers were determined as accurately as possible.

The times of flow with water were determined with the three instruments

at 15, 18, 20, 22, 25, 27 and 30°. In terms of Reynolds' criterion the velocities of flow varied between 25 and 63.

The resulting data were compared with previously determined viscosities of water in a manner to show any variations in m. It was found that any of the three viscometers reproduced the Bureau of Standards data for water on the assumption that *m* was zero. No evidence was found for believing that *m* changed in value due to the configuration of the capillary ends.

These results were discussed in relation to Dorsey's interpretation of m.

The viscosities of urethan solutions up to 4.5 moles/1000 g. of solution were determined at 20 and 25° for future use in standardizations. These data were given in reference to the Bureau of Standards data for water.

TUFTS COLLEGE (57), MASSACHUSETTS

[CONTRIBUTION FROM THE PEARSON CHEMICAL LABORATORY OF TUFTS COLLEGE]

THE VISCOSITIES OF SEVERAL AQUEOUS SOLUTIONS OF ORGANIC SUBSTANCES. II

BY H. M. CHADWELL AND B. ASNES

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A study of the compressibilities and volume changes upon solution of several organic substances in water[1] has shown that with these properties, the effect of a change in the polymerization of the solvent is most apparent. The viscosities of these same solutions determined at 25°[2] showed no effect that could be ascribed to such a change in molecular state, for it was found that although the solutes had viscosities very much less than water, the aqueous solutions possessed a viscosity greater than water. If a depolymerization of the solvent was brought about by the presence of solute, the viscosity should be decreased, for the depolymerized water is supposed to possess a lower viscosity.[3] Determinations made at a lower temperature, where the water is supposedly richer in polymer, might show this effect more vividly. As a consequence, one of the viscometers (Viscometer I) whose standardization was described in the preceding paper, was used to measure this property at 10° of aqueous solutions of diethyl ether, methyl and ethyl acetates and urethan.

It has been reported[4] that aqueous solutions of urea show "negative viscosity," or viscosity less than water. Since this seems to be an exception to the general rule that aqueous solutions of non-electrolytes possess a viscosity greater than water, determinations were made at 5, 10,

[1] Richards and Chadwell, THIS JOURNAL, 47, 2283 (1925).

[2] Chadwell, *ibid.*, 48, 1912 (1926).

[3] See, for instance, Tammann and Rabe, *Z. anorg. allgem. Chem.*, **168**, 73 (1927).

[4] Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., 1922, p. 179. The reference to Mutzel seems to be an error.

15, 20 and 25°. No evidence was found within the range of concentrations studied that this was an exceptional substance.

Purification of Materials

Water.—Thrice distilled water, similar to that described in the previous paper, was used for these experiments.

Methyl and Ethyl Acetates.—Samples of esters which had been purified for a previous investigation[2] were shaken with solid sodium carbonate, treated with phosphorus pentoxide, and distilled in an all glass apparatus consisting of a Richards–Barry flask and condenser. Practically all of the material boiled at the same temperature as in the first purification, 77.15" for the ethyl ester and 57.2" for the methyl acetate (760 mm.). Their densities ($d_4^{10}{}_{\text{vac.}}$) were 0 9127 and 0.9466, respectively.[5]

Urea.—Urea of the highest purity from a reliable commercial source was crystallized twice from water, the saturated solutions being prepared at 60° and the crystals separated and washed in a centrifuge. It was dried for several days in a desiccator over sodium hydroxide, dried in an oven at 50° and then kept in a desiccator over sodium hydroxide until used. The urea used in the 5, 10 and 15% solutions was purified in the same way from material of a different source.

The crystallizations were carried out rapidly and at comparatively low temperatures because of the possibility of changing urea into ammonium cyanate. Fawsitt[6] showed that such a change, caused by heating a solution at 100" for an hour, would increase the relative viscosity slightly.

Urethan.—The urethan was purified in a similar manner to urea, twice crystallized from water with centrifuging, washing and drying.

Apparatus and Technique

The apparatus used in these experiments has been described in the foregoing paper. (Viscometer I, having a capillary radius of 0.241 mm., was used throughout.) All of the precautions for accurate work were observed; for instance, the solution was moved from the lower to the higher bulb in the viscometer by an application of pressure of dry air rather than by suction.

The temperature of the thermostat was determined by a tenth degree thermometer that had been standardized by the Bureau of Standards. Variations of temperature were measured by a Beckmann thermometer. At 5° the thermostat remained constant to ±0.01°; at higher temperatures it was more constant, ±0.003°.

The solutions were made up by weight immediately preceding the experiment in all cases except the 5, 10 and 15% solutions of urea; in the latter cases a large amount of solution was prepared and used at the different temperatures.

The densities were determined in 10-cc. Ostwald pycnometers which were provided with a small bulb beyond the graduation scratch on the side arm. All densities were calculated to the vacuum standard.

Experimental Results

The experimental results are given in Tables I and II.

Table I contains the results for various solutions at approximately 10°, while Table II shows how urea solutions change with temperature. In

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[5] These values are in excellent agreement with those obtained by interpolation among the data of Young and Thomas, J. Chem. *Soc.*, **63,** 1191 (1893).

[6] Fawsitt, *Proc. Roy. Soc.* Edinburgh, *25,* 52 (1904). The equilibrium has been studied by Walker and Hambly, J. Chem. *Soc.*, **67, 746** (1895).

TABLE I

THE RELATIVE VISCOSITIES OF VARIOUS AQUEOUS SOLUTIONS AT 9.98°

%	m	t	$\rho_{vac.}$	η_r
		Methyl Acetate		
0	0	602.2	0.9997	1.000_0
3.857	.542	660.8	1.0016	1.099_4
5.768	.827	688.2	1.0025	1.146_0
9.048	1.344	731.2	1.0039	1.219_3
13.047	2.026	779.8	1.0055	1.302_4
14.417	2.275	792.6	1.0060	1.324_5
20.776	3.542	840.0	1.0080	1.406_5
23.117	4.061	849.4	1.0090	1.423_6
98.901		212.1	0.9485	0.334_1
100.000		207.4	.9466	$.326_1$
		Ethyl Acetate		
0.522	0.060	608.1	0.9998	1.009_9
2.613	.305	651.5	1.0001	1.082_3
2.845	.333	654.4	1.0002	1.087_2
3.206	.376	664.2	1.0002	1.103_5
4.804	.573	694.4	1.0005	1.154_0
6.683	.813	733.2	1.0008	1.218_9
98.216		267.6	0.9158	0.407_0
100.000		256.4	.9115	$.388_7$
		Diethyl Ether		
1.031	0.141	627.9	0.9979	1.040_8
1.408	.193	638.9	.9974	1.058_4
2.894	.402	680.8	.9951	1.125_3
5.751	.824	770.5	.9911	1.268_4
100.000		165.3	.7256	0.199_1
		Urea		
1.676	0.284	602.1	1.0044	1.004_5
4.116	.715	604.9	1.0111	1.016_0
4.162	.723	606.0	1.0113	1.018_0
8.078	1.464	614.1	1.0226	1.043_1
14.094	2.732	629.9	1.0399	1.088_1
19.488	4.031	652.8	1.0556	1.144_7
		Urethan		
2.213	0.266	630.1	1.0027	1.049_5
6.553	0.787	693.2	1.0086	1.161_4
8.812	1.085	724.5	1.0117	1.217_5
13.986	1.826	817.7	1.0187	1.383_7
25.643	3.872	996.7	1.0331	1.710_5

Table I the first column contains the percentage of solute by weight; the second, the number of moles per 1000 g. water (the molecular weights used were methyl acetate, 74.048; ethyl acetate, 88.064; ethyl ether, 74.077; urethan, 89.064; urea, 60.048); the third, the density in vacuum, and the

TABLE 11

THE RELATIVE VISCOSITIES OF AQUEOUS SOLUTIONS OF UREA AT VARIOUS TEMPERATURES

Concentration of Solutions

Solution	A	B	C
% Urea by weight	5.00	10.00	15.00
Moles/1000 g. H_2O	0.876	1.850	2.939

	5.04°			9.98°		
No.	t	$\rho_{vac.}$	η_r	t	$\rho_{vac.}$	η_r
H_2O	698.7	1.0000	1.000$_0$	602.2	0.9997	1.000$_0$
A	701.3	1.0150	1.018$_8$	605.9	1.0140	1.0206
B	709.7	1.0296	1.045$_8$	617.3	1.0283	1.054$_4$
C	726.7	1.0444	1.086$_3$	631.4	1.0428	1.093$_8$
	15.04°			20.01°		
H_2O	523.4	0.9991	1.000$_0$	462.3	0.9982	1.000$_0$
A	531.8	1.0132	1.030$_4$	471.0	1.0120	1.0329
B	542.4	1.0273	1.065$_6$	482.0	1.0257	1.0714
C	557.6	1.0415	1.110$_6$	496.4	1.0396	1.1183

25.07°

	t	ρ_{vac}	η_r
H_2O	410.6	0.9971	1.000$_0$
A	420.3	1.0106	1.037$_6$
B	430.4	1.0240	1.076$_6$
C	444.4	1.0376	1.126$_4$

fourth relative viscosity. The headings of the columns in Table II have the same meanings. The relative viscosity was calculated by the formula

$$\eta_r = \frac{t_s \rho_s}{t_o \rho_o}$$

Here the subscript *s* refers to the solution while o refers to water. The density (ρ) is that in air, obtained from the value of density in vacuum given in the table, by subtracting the weight of 1 ml. of air (0.0012).

The use of the simple formula for calculating viscosity is justified by the fact that in the preceding paper it was shown that this viscometer would reproduce the viscosities of water as accepted by the Bureau of Standards over the temperature range of 15 to 30° when the value of *m* (Formula 4, preceding paper) was taken as zero. From Dorsey's analysis of the flow of liquids through tubes, it is logical to assume that this same condition would be fulfilled for flows of smaller velocity.[7]

[7] The absolute viscosities are not reported for the reason that the viscosities of water at 10 and 5° as calculated from the formula $\eta = 2.1851\, t \times 10^{-5}$ (obtained during the standardization of this viscometer and reported in the preceding paper) and the time of flow as given in Table II, are not in good agreement with the previously published values for water. The values are as follows, expressed in centipoises

	5.04°	9.98°
Calculated	1.5249	1.3139
Bingham and Jackson (B. of S.)	1.517$_0$	1.3085
"International Critical Tables"	1.517$_0$	1.3105

The times of flow for water are in agreement with those reported in the preceding

Discussion of Results

The relative viscosities of the urea solutions at different temperatures given in Tables I and II are plotted against moles per 1000 g. water in Fig. 1. The data are consistent except for the 5% solution at 25° which is slightly high (about 0.3%) and the 15% solution at 10° which is low (about 0.2%).

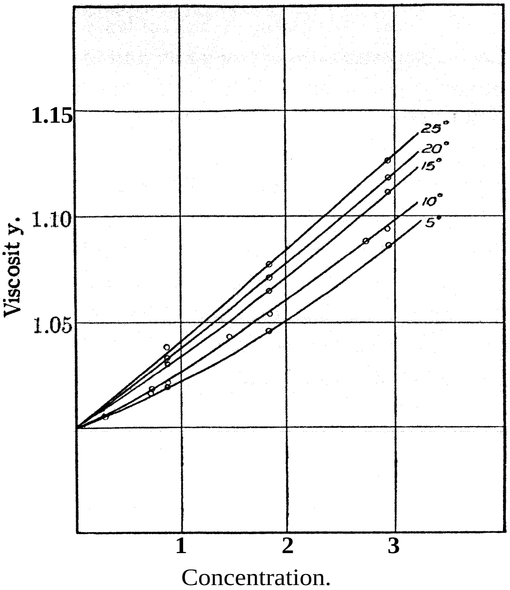

Fig. 1.—The viscosities of aqueous urea solutions at 5, 10, 15, 20 and 25°. The relative viscosities are plotted as ordinates, the concentrations expressed in moles per kg. of water as abscissa.

Rudolf[8] has reported determinations at 25° which show a minimum in the viscosity curve at a value less than that of water, but Fawsitt[9] could not verify his results using very pure urea. Ranken and Taylor[10] redetermined the viscosity of urea solutions at temperatures ranging from 8 to 45° and found that only in one solution was the viscosity less than that of water, namely, in the most dilute solution (0.03125 mole/liter) at 8°, the relative viscosity was 0.9985. This value was reported as reproducible.

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paper with the exception of that for 20" (462.3 seconds instead of 461.3). Since this difference may have been caused by an accidental shifting of the viscometer in the holder, the time determined at the time of the experiments with the solutions was used in the calculations. An interval of approximately a year separated the two sets of experiments.

[8] Rudolf, *Z. physik. Chem.*, *43*, 257 (1903).

Moles/liter	0.937	0.469	0.234	0.117	0.058
η_r	1.010	1.002	.996	.993	.995

[9] Fawsitt, *Proc. Roy. Soc. Edinburgh*, **25**, 52 (1904).

Moles/liter	0.10	0.25	0.5	1.0	2.0
η_r	1.005	1.012	1.024	1.045	1.089

[10] Ranken and Taylor, *Trans. Roy. Soc. Edinburgh*, **45*ii***, 397 (1906).

	Moles/liter	0.03125	0.125	0.25	0.50	1.0
η_r	8"	.09985	1.0012			
	15°			1.0085	1.0150	1.0325
	25°	1.0020	1.0050			
	30°			1.0113	1.0210	1.0443

Our results are slightly greater at 15° than those determined by Ranken and Taylor; at 20° they are in good agreement with those of Öholm;[11] at 25° they are considerably greater than those of Dunstan and Mussell,[12] up to a concentration of 2.5 moles/kg. of H_2O, and then they are smaller. The viscosities of supersaturated solutions of urea have been reported recently by Taimni.[13]

The curves in Fig. 1 include no evidence for concluding that urea solutions show "negative viscosity"[14]—viscosities lower than that of water. Certainly there is no such phenomenon as exhibited by certain salts. For example, the concentration of ammonium nitrate must be approximately 18% at 25° before the viscosity of the solution exceeds that of water. Bingham[15] has recommended the term "negative curvature" in referring to fluidity-concentration curves, to replace "negative viscosity." The terms are not synonymous, for it is evident that the fluidity curves for urea solutions would show negative curvature. The viscosities of very dilute solutions, preferably at low temperatures, were not investigated because of the necessity of a more refined method of measuring the time of flow.

The experimental results for all of the solutions are represented in Fig. 2, where the viscosity relative to water is plotted as ordinates and the moles of solute per 1000 g. of water as abscissa. There are also included the data for these solutions previously determined[16] at 25°. As would be expected, the relative positions of the curves for the various solutions are the same at 10° as at 25°, the ethyl ether solutions showing the greatest relative viscosity. The solutions of ethyl ether, ethyl and methyl acetates, and urethan have a greater relative viscosity at 10° than at 25°, while urea solutions are opposite, having a viscosity greater at 25° than at 10°. Furthermore, the viscosities of ether and ethyl acetate solutions are linear functions

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[11] Öholm, through "International Critical Tables," McGraw–Hill Book Co., Inc., 1929, Vol. V, p. 22.

Moles/liter.....	0.25	0.50	1.0	2.0	4.0	8.0
Moles/kg. H_2O..	.25	.52	1.08	2.33		
η_r..............	1.010	1.022	1.039	1.088	1.215	1.655

[12] Dunstan and Mussell, through "International Critical Tables," Ref. 11.

Wt. %....................	1.02	8.13	11.89	15.47	23.12
Moles/kg. H_2O.............	0.18	1.46	2.24	3.08	
η_r.........................	1.005	1.054	1.087	1.162	1.221

[13] Taimni, *J. Phys. Chem.*, 33, 52 (1929).

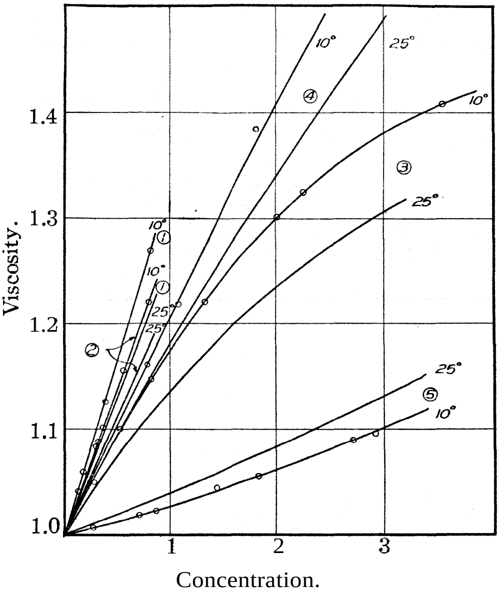
[14] See Rabinovich, THIS JOURNAL, 44, 954 (1922); Taylor and Moore, *Proc. Roy. Soc. Edinburgh*, 28, 461 (1907); Taylor, *ibid.*, 25, 227 (1904). Wagner and Mühlenbein, *Z. physik. Chem.*, 46, 872 (1903), have shown that negative viscosity is exhibited by certain organic substances, for instance, cyanobenzene in alcohol.

[15] Bingham, Ref. 4, p. 178.

[16] Chadwell, Ref. 2. The values of relative viscosity were calculated from the value of η_I given on p. 1918, for the viscometer was very similar to that used in the present investigation.

of the concentration expressed in the units chosen, while methyl acetate produces a convex curve and urea a concave. If the liquids were soluble in water in all proportions, the resulting curves would all show maxima, for the viscosities of the pure liquids are all very much smaller than that of water.[17] Urea, on the other hand, is a solid, and as the concentration increases, the viscosity of the solute has a more pronounced effect.

In discussing the data determined at 25° it was shown that not only was there a connection between the volume of the dissolved molecules, but that there was a very close connection between the change in viscosity and the change in volume, calculated as the contraction in ml. which took place upon the formation of one liter of solution. When a large contraction took place, the viscosity of the solution would be comparatively great. A similar hypothesis has been developed more extensively by McLeod,[18] who postulated that the viscosity of a mixture as well as of a pure liquid is a function of the free space; that the increase in viscosity upon adding a solute is caused principally by the contraction, which has an effect similar to cooling the material. It is interesting, therefore, to see how this property of changing volume on solution changes with temperature. The necessary calculations could be made from the density data. Such data are summarized in Table III and shown graphically in Fig. 3.



1, Ether; 2, ethyl acetate; 3, methyl acetate; 4, urethan; 5, urea.

Fig. 2.—The viscosities of aqueous solutions of ethyl ether, ethyl acetate, methyl acetate, urethan and urea at 10 and 25°. The relative viscosities are plotted as ordinates, the concentrations expressed in moles per kg. of water as abscissas.

The contractions given in the above table were calculated from the densities recorded in Table I for all of the liquids. Those for urea solutions

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[17] Solutions of dioxane and water, soluble in all proportions, produce a maximum. Herz and Lorentz, Z. *physik.* Chem., A140, 408 (1929).

[18] McLeod, *Trans. Faraday Soc.*, 19, 6 (1923); 19, 17 (1923); 20, 348 (1924); **21,** 151 (1925). A full discussion and several suggestions are made in Hatschek's "Viscosity of Liquids," D. Van Nostrand Company, New York, 1928.

TABLE III

CONTRACTIONS TAKING PLACE UPON SOLUTION. CHANGE IN VOLUME (ML.) UPON FORMATION OF ONE LITER OF SOLUTION

Moles/kg. H_2O	0.2	0.4	0.6	0.8	1.0	1.5	2.0	2.5
			Ethyl Ether in Water					
25°	3.0	6.5	10.1	14.0				
10"	3.0	6.3	9.4	12.5				
			Ethyl Acetate in Water					
25°	1.9	3.7	5.5	7.2				
10"	1.9	3.7	5.6	7.4				
			Methyl Acetate in Water					
25° 10°	1.6	3.1	4.5	6.8	7.1	10.2	13.1	15.5
			Urea in Water					
25°		(0.6)			1.3	1.8	2.1	2.5
20°		(.8)			1.7	2.2	2.8	3.2
15°		(.9)			2.0	2.8	3.4	4.0
10°		(1.0)			2.2	3.1	3.8	4.6
5°		(1.3)			3.0	4.0	4.9	5.6

are the volume changes for solid urea dissolved in water. The densities of solid urea were found by interpolation from the data of Dewar given in the "International Critical Tables."[19] The contraction for each of the solutions was calculated and plotted, and the above values found by interpolation.

The volume changes for urethan solutions were also calculated, for 10, 20 and 25°, making use of the data in the preceding paper, and Block's[20] data for both solid urethan and the supercooled liquid urethan. If the former (for the solid) are used, an expansion results; if the latter, a contraction which decreases with an increase in temperature.[21] The volume

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[19] "International Critical Tables," Vol. III, p. 45. The data used were

t, °C.	5	10	15	20	25
d_4^t	1.3215	1.3204	1.3194	1.3184	1.3173

The slopes of the curves seem to show that the specific volumes accepted for the urea are too large, that the calculated contractions are consequently too large. No data are available for estimating the specific volume of liquid urea at these temperatures.

[20] Block, *Z. physik.* Chem., 78,397 (1912).

[21] Contraction on formation of urethan solutions (interpolated data)

Moles/kg. H_2O	10°	20°	25°
1.0	4.1 (−0.1)	3.6 (−0.7)	3.3 (−1.1)
2.0	7.2 (− .5)	6.3 (−1.7)	5.9 (−2.3)
3.0	9.5 (−1.5)	8.3 (−3.0)	7.7 (−3.8)

The figures given in parentheses are expansions calculated from the densities of solid urethan; the others are contractions as calculated from supercooled liquid. The data used for the volume of 1 g. of urethan, either liquid or solid, are as follows (interpolated or extrapolated)

	10°	20°	25°
Liquid	0.9149	0.9230	0.9271
Solid	,8641	.8704	.8736

changes upon solution of urethan at 20° have been studied by Richards and Palitzsch.[22] They have pointed out that the expansion upon the solution of solid is probably caused by a large expansion due to the breaking up of the crystalline material counteracted by a contraction caused by the change in polymerized water. Our conclusion drawn from this interpolation is that the specific volume of molten urethan should be used to calculate the contraction, but its value is so uncertain, because of the large extrapolation, that little confidence can be placed in the results; consequently they are not plotted in Fig. 3.

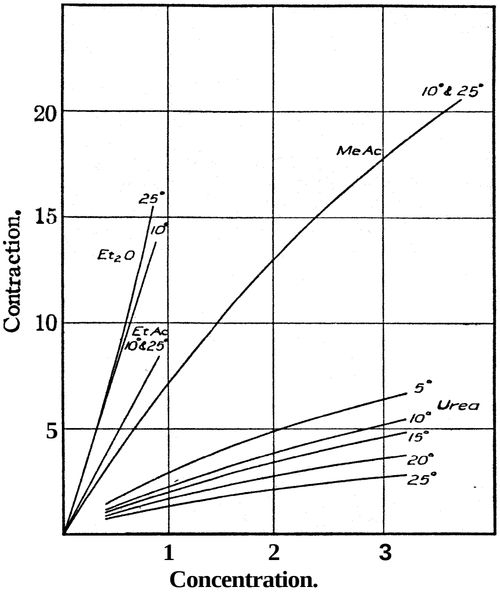

Fig. 3.—The contraction upon formation of aqueous solutions of ethyl ether, ethyl acetate and methyl acetate at 10 and 25°, and of urea at temperatures between 5 and 25°. The decreases in volume (ml.) upon formation of 1 liter of solution are plotted as ordinates, the concentrations expressed in moles per kg. of water as abscissas.

That the volume changes upon solution of the esters are the same at 10 and 25°, within the experimental error, is a surprise. One would expect a greater contraction at the lower temperature if it is assumed that the ester causes a depolymerization of the water, for water must be more highly polymerized at the lower temperature. More accurate density determinations probably would show slight differences.

The changes in volume on formation of solutions are interesting, irrespective of their bearing upon the question of viscosity. The method of representing concentration as moles of solute per 1000 g. of water is so chosen as to represent the effect of relative numbers of molecules of different solutes upon the same quantity (possibly different number of molecules) of water. The contraction is the greatest for ether, and successively less for ethyl acetate, methyl acetate and urea. This confirms the hypothesis that[1] the cohesive forces and internal pressures existing in the liquids play a large part in determining the volume of the systems. The forces under which the molecules of the various solutes exist in solutions of equivalent concentrations are probably about the same, and yet those forces are very different in

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[22] Richards and Palitzsch, This Journal, 41, 60 (1919). Also Richards and Chadwell, *ibid.*, 47, 2283 (1925).

the pure liquids. When the molecular forces existing in a liquid are weak (small internal pressure), the liquid is light and volatile and possesses a large coefficient of compressibility. If such a liquid is distributed in a second liquid of greater internal forces, it would be exepcted that the volume would not be so large and that the extent to which a contraction took place would depend upon the difference in magnitude of the internal pressures. In the particular cases in question, the magnitudes of the contraction are in the same order as the coefficients of compressibility. The average compressibilities over the pressure range of 100–300 megabars at 20° are: ether 130, ethyl acetate 90 and methyl acetate 88.[1,23]

It is to be noticed that the viscosity and contraction curves in Pigs. 2 and 3 for the different solutes are in the same relative positions for either 10 or 25°; but this correlation does not hold when a single solute is considered, showing that the change in volume is not the only determining factor of the viscosity. The urea solutions, for instance, show the greater relative viscosity at the higher temperature, while the contractions are greater at the lower temperature. This can be explained by postulating that the decrease in viscosity due to the depolymerization of the water, taking place to a greater extent at the lower temperatures, more than balances the tendency to increase the viscosity caused by the contraction. Such a counterbalancing of effects is not apparent in the positions of the curves for other solutes. In support of this hypothesis it should be pointed out that the aqueous urea solutions are more nearly ideal than the others: the internal pressures of the pure substances are very nearly alike, their mutual solubility is great, and the formation of solutions is accompanied by a small volume change.

Viscosity curves of binary liquid mixtures which show maxima have commonly been explained by assuming compound formation. If this is the real explanation, solvation is a very general phenomenon—more general than other properties of solutions would lead us to believe. The relative viscosity of all of these solutions (except urea) diminishes with an increase in temperature. In the case of aqueous solutions of salts[24] this is found to occur only in those solutions which contain highly hydrated materials, and is supposed to be due to the thermal decomposition of the hydrates.

In the cases of our particular solutes, freezing point measurements[25] have been made and the solutions found to be normal. Kendall and Harrison have interpreted the normal depressions caused by esters to mean that

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[23] Richards, Stull, Mathews and Speyers, THIS JOURNAL, 34, 971 (1912).

[24] Rabinovich, *ibid.*, 44, 956 (1922). Aqueous salt solutions show no correlation between negative viscosity and contraction.

[25] "International Critical Tables," Vol. IV, p. 262; Kendall and Harrison, ***Trans. Faraday Soc.***, 24, 588 (1928).

hydrates are formed which counterbalance negative deviations from Raoult's law arising from the fact that the solutions are not perfect.

The development of our knowledge of liquids from the electrical standpoint is only beginning, and yet enough progress has resulted to show that such a property as viscosity may well be considered from this point of view. Jones and Dole,[26] for instance, have shown that the viscosity of dilute salt solutions can best be represented by a formula which takes into account the effect of interionic forces. For binary mixtures of different liquids the shape of the viscosity–concentration curve depends upon the electrical nature of the molecules. If both of the components are non-polar, or one is dipolar (in the sense used by Debye) the curve is concave, but if both components are dipolar, the curve is convex.[27] Our liquid mixtures are composed of dipolar molecules, their electric moments[28] in the liquid state being: water 1.8, ether 1.24, methyl acetate 1.67 and ethyl acetate 1.74 (all X 10^{18}). These polar molecules in solution would be orientated[29] by the electrostatic field produced by other molecules into more or less orderly arrangements which might very well be manifested by an increase in the relative viscosity, as well as a contraction in volume. Furthermore, an increase in temperature reduces this orientation and the viscosity would become less, as is shown by the experimental data. A quantitative analysis of this contributing effect must await more extensive determinations of dielectric constants and the development of the theory of viscosity of liquids.

We wish to express our gratitude to the Elizabeth Thompson Science Fund for financial aid in this investigation.

Summary

The viscosities of aqueous solutions were determined at 10° of diethyl ether, methyl acetate, ethyl acetate, urethan and urea. In addition, measurements were made on urea solutions at 5, 15, 20 and 25°.

The contractions on solution of these substances were calculated from the densities, and the connection between these two properties was discussed.

Aqueous solutions of urea did not possess viscosities less than water at any of the concentrations studied, although the curvature of the viscosity–concentration curve was found to be positive. These solutions do not seem to be exceptions to the rule that aqueous solutions of non-electrolytes pos-

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[26] Jones and Dole, THIS JOURNAL, 51, 2950 (1929); Falkenhagen and Dole, *Physik. Z.*, 30, 611 (1929).

[27] Shown empirically by Errera, *Z. physik. Chem.*, **140A**, 273 (1929).

[28] Williams, *Chem. Rev.*, 6, 595 (1929). The moments of urea and urethan have not been determined, so far as we know.

[29] See Langmuir, *ibid.*, 6, 459 (1929), and Smyth, *ibid.*, 6, 560 (1929).

sess a viscosity greater than that of water, irrespective of the viscosity of the solute.

The effect of depolymerization of water upon the property of viscosity was no more apparent at 10° than at 25°, except possibly in the case of the urea solutions.

The results were discussed from the point of view of compound formation and orientation of polar molecules.

TUFTS COLLEGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY IN THE LABORATORIES OF PHYSIOLOGY, HARVARD MEDICAL SCHOOL]

THE TITRATION CONSTANTS OF MULTIVALENT SUBSTANCES

BY ALEXANDER L. VON MURALT

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It has long been known that the titration curve of a multivalent acid resembles that of a mixture of monovalent acids. Based upon the apparent identity of these two classes of titration curves, as judged by experiment, H. S. Simms[1] has developed equations which correlate the apparent with the true dissociation constants of a multivalent acid. The equations are given for a divalent and trivalent acid, and the same considerations readily yield the equations for any number of valencies.

Apparently without knowledge of Simms' contribution, H. H. Weber[2] has recently treated this problem in a very similar manner. The equations which he obtains are more restricted and not as generally applicable as those developed by Simms, since he introduced the further assumption that the titration curve of the multivalent acid resembles that of a single monovalent acid. In discussing these two papers in our seminar, it became apparent that the assumption of resemblance is unnecessary, for the general equations of Simms may be obtained by a purely mathematical transformation of the classical dissociation equations given by the mass law.[3] This mathematical transformation yields no equations other than those developed by Simms, but in that the same relations are obtained without any assumption, the behavior of multivalent substances as described by the classical equations is vested with a slightly altered interpretation which rendered it desirable to communicate the calculations.

The classical dissociation constants for the n steps of dissociation of a multivalent acid may be written

[1] H. S. Simms, THIS JOURNAL, 48, 1239 (1926).

[2] H. H. Weber, Biochem. Z., 189, 381 (1927).

[3] In a previous seminar Professor Scatchard was able to derive Weber's equations on the assumption that the probability of dissociation was the same for each group, and independent of the number of groups dissociated.

$$
\begin{aligned}
K_1' &= \frac{[\mathrm{H}][\mathrm{H}_{n-1}\mathrm{A}']}{[\mathrm{H}_n\mathrm{A}]} \\
K_1'K_2' &= \frac{[\mathrm{H}]^2[\mathrm{H}_{n-2}\mathrm{A}'']}{[\mathrm{H}_n\mathrm{A}]} \\
&\vdots \\
K_1'K_2'\ldots K_n' &= \frac{[\mathrm{H}]^n[\mathrm{A}^{n-}]}{[\mathrm{H}_n\mathrm{A}]}
\end{aligned}
\qquad (1)
$$

The dissociation of a monovalent as well as of a multivalent acid can be described in terms of the following ratios

$$(1)\quad \frac{\text{Concentration of dissociated hydrogen ions}}{\text{Concentration of undissociated hydrogen ions}} = \alpha$$

$$(2)\quad \frac{\text{Concentration of dissociated hydrogen ions}}{\text{Equivalent concentration}} = \beta$$

$$(3)\quad \frac{\text{concentration of undissociated hydrogen ions}}{\text{Equivalent concentration}} = \rho$$

In terms of the classical dissociation constants these ratios take the form

$$\alpha = \frac{\dfrac{K_1'}{[\mathrm{H}]} + 2\dfrac{K_1'K_2'}{[\mathrm{H}]^2} + \ldots\ldots + (n-1)\dfrac{K_1'K_2'\ldots K_{n-1}'}{[\mathrm{H}]^{n-1}} + n\dfrac{K_1'K_2'\ldots K_n'}{[\mathrm{H}]^n}}{n + (n-1)\dfrac{K_1'}{[\mathrm{H}]} + (n-2)\dfrac{K_1'K_2'}{[\mathrm{H}]^2} + \ldots\ldots + \dfrac{K_1'K_2'\ldots K_{n-1}'}{[\mathrm{H}]^{n-1}}} \qquad (2)$$

$$\beta = \frac{1\dfrac{K_1'}{[\mathrm{H}]} + 2\dfrac{K_1'K_2'}{[\mathrm{H}]^2} + \ldots\ldots + (n-1)\dfrac{K_1'K_2'\ldots K_{n-1}'}{[\mathrm{H}]^{n-1}} + n\dfrac{K_1'K_2'\ldots K_n'}{[\mathrm{H}]^n}}{n\left(1 + \dfrac{K_1'}{[\mathrm{H}]} + \dfrac{K_1'K_2'}{[\mathrm{H}]^2} + \ldots\ldots + \dfrac{K_1'K_2'\ldots K_{n-1}'}{[\mathrm{H}]^{n-1}} + \dfrac{K_1'K_2'\ldots K_n'}{[\mathrm{H}]^n}\right)} \qquad (3)$$

$$\rho = \frac{n + (n-1)\dfrac{K_1'}{[\mathrm{H}]} + (n-2)\dfrac{K_1'K_2'}{[\mathrm{H}]^2} + \ldots\ldots + \dfrac{K_1'K_2'\ldots K_{n-1}'}{[\mathrm{H}]^{n-1}}}{n\left(1 + \dfrac{K_1'}{[\mathrm{H}]} + \dfrac{K_1'K_2'}{[\mathrm{H}]^2} + \ldots\ldots + \dfrac{K_1'K_2'\ldots K_{n-1}'}{[\mathrm{H}]^{n-1}} + \dfrac{K_1'K_2'\ldots K_n'}{[\mathrm{H}]^n}\right)} \qquad (4)$$

These rather complicated expressions[4] can be simplified considerably by a mathematical transformation, known as separation into *partial fractions.* The rational algebraic expression $F(x)/\Phi(x)$ can be expressed as the sum of partial fractions, which have the several factors of $\Phi(x)$ as denominators and which have constants for numerators. In order to show how Equations **2,** **3** and 4 can be separated into partial fractions, the detailed calculation for **3** is given here. With appropriate modifications the same method **can** be applied to **(2)** and (4).

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[4] The terms in the mass law equations have, for mathematical convenience, been written as stoichiometrical concentrations rather than as activities. Activity coefficients could, of course, be introduced into these series.

The first step which is taken is to render Equation 3 more convenient for further transformation by multiplying both numerator and denominator by $[\mathrm{H}]^n$

$$\beta = \frac{1K'_1[\mathrm{H}]^{n-1} + 2K'_1K'_2[\mathrm{H}]^{n-2} + \ldots\ldots + (n-1)\,K'_1K'_2\ldots K'_{n-1}[\mathrm{H}] + n\,K'_1K'_2\ldots K'_n}{n\,([\mathrm{H}]^n + K'_1[\mathrm{H}]^{n-1} + K'_1K'_2[\mathrm{H}]^{n-2} + \ldots\ldots + K'_1K'_2\ldots K'_{n-1}[\mathrm{H}] + K'_1K'_2\ldots K'_n} \tag{3a}$$

In (3a) the denominator has the form of the expansion of the general polynomial

$$(\kappa_1 + x)\,(\kappa_2 + x)\,(\kappa_3 + x)\ldots\ldots(\kappa_n + x) \tag{4a}$$

which in the expanded form can be written

$$x^n + \Sigma\kappa_1x^{n-1} + \Sigma\kappa_1\kappa_2x^{n-2} + \Sigma\kappa_1\kappa_2\kappa_3x^{n-3} + \ldots + \Sigma\kappa_1\kappa_2\kappa_3\ldots\kappa_n \tag{4b}$$

The symbol $\Sigma\kappa$ represents the sum of the elements $\kappa_1 + \kappa_2 + \kappa_3 + \ldots\kappa_n$, $\Sigma\kappa_1\kappa_2$ the sum of the combinations without repetition of the elements $\kappa_1, \kappa_2, \ldots\kappa_n$ taken two at a time, $\Sigma\kappa_1\kappa_2\kappa_3$ the sum of the combinations without repetition of the elements $\kappa_1, \kappa_2, \ldots\kappa_n$ taken three at a time, and so forth.

Comparison of Equation 4b with the denominator in (3a) shows that both are identical except for the factors of corresponding powers of [H] and x. By equating the undeterminate factors of corresponding powers of [H] and x, n equations are obtained which define completely the new factors κ_1, $\kappa_2, \ldots\kappa_n$ in terms of the old factors $K'_1, K'_2, \ldots K'_n$.

$$\begin{aligned}
K'_1 &= \Sigma\kappa_1 &&= \kappa_1 + \kappa_2 + \kappa_3 + \ldots\ldots\kappa_n \\
K'_1K'_2 &= \Sigma\kappa_1\kappa_2 &&= \kappa_1\kappa_2 + \kappa_1\kappa_3 + \ldots + \kappa_1\kappa_n + \ldots\kappa_{n-1}\kappa_n \\
K'_1K'_2K'_3 &= \Sigma\kappa_1\kappa_2\kappa_3 &&= \kappa_1\kappa_2\kappa_3 + \kappa_1\kappa_3\kappa_4 + \ldots\ldots\kappa_{n-2}\kappa_{n-1}\kappa_n \\
&\ldots\ldots && \ldots\ldots \\
&\ldots\ldots && \ldots\ldots \\
K'_1K'_2\ldots\ldots K'_n &= \Sigma\kappa_1\kappa_2\ldots\kappa_n &&= \kappa_1\kappa_2\kappa_3\ldots\ldots\kappa_n
\end{aligned} \tag{5}$$

Consequently we may write

$$\begin{aligned}
&n\,([\mathrm{H}]^n + K'_1[\mathrm{H}]^{n-1} + K'_1K'_2[\mathrm{H}]^{n-2} + \ldots\ldots + K'_1K'_2\ldots K'_{n-1}[\mathrm{H}] + K'_1K'_2\ldots K'_n) \equiv \\
&\equiv n\,([\mathrm{H}]^n + \Sigma\kappa_1[\mathrm{H}]^{n-1} + \Sigma\kappa_1\kappa_2[\mathrm{H}]^{n-2} + \ldots\ldots + \Sigma\kappa_1\kappa_2\ldots\kappa_{n-1}[\mathrm{H}] + \Sigma\kappa_1\kappa_2\kappa_3\ldots\kappa_n) \equiv \\
&\equiv n\,((\kappa_1 + [\mathrm{H}])(\kappa_2 + [\mathrm{H}])\cdot(\kappa_3 + [\mathrm{H}])\ldots\ldots(\kappa_n + [\mathrm{H}]))
\end{aligned} \tag{6a}$$

The numerator can also be transformed by means of the same set of Equations (5), yielding the following identity

$$\begin{aligned}
&\frac{1K'_1[\mathrm{H}]^{n-1} + 2K'_1K'_2[\mathrm{H}]^{n-2} + \ldots\ldots + (n-1)\,K'_1K'_2\ldots K'_{n-1}[\mathrm{H}] + n\,K'_1K'_2\ldots K'_n}{n\,([\mathrm{H}]^n + K'_1[\mathrm{H}]^{n-1} + K'_1K'_2[\mathrm{H}]^{n-2} + \ldots\ldots + K'_1K'_2\ldots K'_{n-1}[\mathrm{H}] + K'_1K'_2\ldots K'_n)} \equiv \\
&\equiv \frac{1\,\Sigma\kappa_1[\mathrm{H}]^{n-1} + 2\,\Sigma\kappa_1\kappa_2[\mathrm{H}]^{n-2} + \ldots\ldots + (n-1)\,\Sigma\kappa_1\kappa_2\ldots\kappa_{n-1}[\mathrm{H}] + n\,\Sigma\kappa_1\kappa_2\ldots\kappa_n}{n\,((\kappa_1 + [\mathrm{H}])\,(\kappa_2 + [\mathrm{H}])\,(\kappa_3 + [\mathrm{H}])\ldots\ldots(\kappa_n + [\mathrm{H}])}
\end{aligned} \tag{6b}$$

This transformed expression of (3) may now be separated into partial fractions and we may write

$$\begin{aligned}
&\frac{\Sigma\kappa_1[\mathrm{H}]^{n-1} + 2\,\Sigma\kappa_1\kappa_2[\mathrm{H}]^{n-2} + \ldots\ldots + (n-1)\,\Sigma\kappa_1\kappa_2\ldots\kappa_{n-1}[\mathrm{H}] + n\,\Sigma\kappa_1\kappa_2\kappa_n}{n\,((\kappa_1 + [\mathrm{H}])\,(\kappa_2 + [\mathrm{H}])\,(\kappa_3 + [\mathrm{H}])\ldots\ldots(\kappa_n + [\mathrm{H}]))} \equiv \\
&\equiv \frac{1}{n}\left(\frac{\kappa_1}{\kappa_1 + [\mathrm{H}]} + \frac{\kappa_2}{\kappa_2 + [\mathrm{H}]} + \frac{\kappa_3}{\kappa_3 + [\mathrm{H}]} + \ldots\ldots + \frac{\kappa_n}{\kappa_n + [\mathrm{H}]}\right)
\end{aligned} \tag{7}$$

The proof that the separation into partial fractions (7) is correct may be obtained by clearing the left and the right side of fractions. Since this procedure is well known to those familiar with partial fractions, it has been omitted.

Applying the same transformation to Equations 2 and 4, corresponding identities are obtained, which are given without the calculation, as the procedure is very much the same as for Equation **3.**

$$\alpha = \frac{\frac{\kappa_1}{\kappa_1+[H]} + \frac{\kappa_2}{\kappa_2+[H]} + \frac{\kappa_3}{\kappa_3+[H]} + \dots\dots + \frac{\kappa_n}{\kappa_n+[H]}}{[H]\left(\frac{1}{\kappa_1+[H]} + \frac{1}{\kappa_2+[H]} + \frac{1}{\kappa_3+[H]} + \dots\dots + \frac{1}{\kappa_n+[H]}\right)} \qquad (2')$$

$$\beta = \frac{1}{n}\left(\frac{\kappa_1}{\kappa_1+[H]} + \frac{\kappa_2}{\kappa_2+[H]} + \frac{\kappa_3}{\kappa_3+[H]} + \dots\dots + \frac{\kappa_n}{\kappa_n+[H]}\right) \qquad (3')$$

$$= \frac{1}{n}\left(\frac{[H]}{\kappa_1+[H]} + \frac{[H]}{\kappa_2+[H]} + \frac{[H]}{\kappa_3+[H]} + \dots\dots + \frac{[H]}{\kappa_n+[H]}\right) \qquad (4')$$

Equations 2′, 3′ and 4′ were derived from (2), (3) and (4) by separation into partial fractions and by introducing a set of new constants $\kappa_1,\kappa_2,\dots.\kappa_n$ for mathematical convenience. If one formulates the fractions α, β, p for a mixture of monovalent acids, with dissociation constants $G'_1,G'_2\dots G'_n$ (using Simms' notation), an identical set of equations is obtained, in which the $G'_1,G'_2\dots G'_n$ replace the constants $\kappa_1,\kappa_2\dots.\kappa_n$.

$$\kappa_1 = G'_1; \quad \kappa_2 = G'_2; \quad \dots\dots \quad \kappa_n = G'_n$$

These constants which have so far been used as a mathematical convenience without any specific meaning attached to them, are therefore the titration constants, and in order not to complicate the nomenclature can be replaced by the titration constants of Simms. They are related to the classical constants by Equation 5, which is, of course, identical with the equation, previously developed by Simms, with the assumption of similarity. In our treatment we have assumed only validity of the classical mass law equations and the result has been derived by mere mathematical transformation of these equations. It follows, therefore, that between the titration curve of a multivalent acid and a mixture of monovalent acids there is no difference. In other words, if the classical dissociation constants of a multivalent acid are known, it is possible to make a mixture of monovalent acids which will give exactly the same titration curve, provided that the individual dissociation constants of the monovalent acids satisfy Equations 5.

Generally one deals with the opposite problem. From the titration curve the titration constants $G'_1,G'_2\dots G'_n$ are experimentally obtained and the classical constants $K'_1,K'_2,\dots K'_n$ can be determined by using Equations 5. We wish again to emphasize that this is only valid in so far as the classical mass law formulation is an accurate description of the facts. Provided this is the case, there is no difference between the dissociation of a multivalent acid and a properly chosen mixture of monovalent acids, and the titration constants are at the same time the "intrinsic" constants of the groups.[5] This relation of course will hold only if the electrostatic work of ionization and the work which is involved in distortion of the molecule are disregarded.

The formulas given by Weber can also be obtained from Equations 5 by assuming that the $G'_1, G'_2, \ldots G'_n$ are all equal, an assumption which Weber has introduced by stating that the titration curve of the multivalent acid resembles that of a single monovalent acid. On this assumption much simpler identities result. Instead of *n* titration constants, one alone is found, therefore

$$G'_1 = G'_2 = G'_3 = \ldots\ldots = G'_n = G'$$

$$\alpha = \frac{G'}{[\mathrm{H}]} \quad (2'') \qquad \beta = \frac{G'}{G' + [\mathrm{H}]} \quad (3'') \qquad \rho = \frac{[\mathrm{H}]}{G' + [\mathrm{H}]} \quad (4'')$$

and the classical dissociation constants are defined by

$$K'_1 = n\,G'; \quad K'_2 = \frac{n-1}{2}G'; \quad K'_3 = \frac{n-2}{3}G'; \quad \ldots; \quad K'_n = \frac{1}{n}G' \qquad (5'')$$

relations which are of course identical with those of Weber. It is obvious that the values of $K'_1, K'_2, \ldots K'_n$ in Equations $5''$ are not independent of each other, since they are all related to definite fractions of one titration constant G^1.

Similar conditions are obtained from the titration data of proteins. Instead of obtaining *n* independent values for the titration constants G', these constants seem to fall into groups of *m* elements which are identical. Therefore only n/m independent values are obtained. This reduces the number of independent Equations 5, relating the titration constants with the classical constants, to n/m. The *n* classical constants K' fall, therefore, into n/m groups of related constants. The case which has been treated by Weber represents grouping of the titration constants G' into one group of identical constants $(n = m)$. For the corresponding group of classical constants K' the following relation is obtained

$$\frac{K'_1}{n} = \frac{2K'_2}{n-1} = \frac{3K:}{n-2} = \ldots\ldots = \frac{nK'_n}{1} \qquad (5a'')$$

The same transformation is applicable in the case of the formula defining the stepwise dissociation of hemoglobin.[6] The equation for the four steps of dissociation is given as

$$\text{Percentage saturation} = \frac{100\gamma'[\mathrm{Hb_4}]\,(K'_1[\mathrm{O_2}] + 2K'_1K'_2[\mathrm{O_2}]^2 + 3K'_1K'_2K'_3[\mathrm{O_2}]^3 + 4K'_1K'_2K'_3K'_4[\mathrm{O_2}]^4)}{4\gamma'[\mathrm{Hb_4}]\,(1 + K'_1[\mathrm{O_2}] + K'_1K'_2[\mathrm{O_2}]^2 + K'_1K'_2K'_3[\mathrm{O_2}]^3 + K'_1K'_2K'_3K'_4[\mathrm{O_2}]^4)} \qquad (9)$$

Separation into partial fractions gives the simpler identity

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[5] E. Q. Adams, THIS JOURNAL, 38, 1503 (1916).

[6] G. S. Adair, *J. Biol. Chem.*, 63, 529 (1925); *Proc. Roy. Soc.*, (London), 109A, 299 (1925); R. M. Ferry and A. A. Green, *J. Biol. Chem.*, 81, 177 (1929).

Percentage saturation =

$$\frac{100\gamma'}{4\gamma'}\left(4-\left(\frac{G'_1}{G'_1+[O_2]}+\frac{G'_2}{G'_2+[O_2]}+\frac{G'_3}{G'_3+[O_2]}+\frac{G'_4}{G'_4+[O_2]}\right)\right) \quad (9a)$$

and the new constants are related to the old constants by the four equations

$$\frac{1}{K'_4} = \Sigma G'_1 = G'_1 + G'_2 + G'_3 + G'_4 \quad (9b)$$

$$\frac{1}{K'_4K'_3} = \Sigma G'_1G'_2 = G'_1G'_2 + G'_1G'_3 + G'_1G'_4 + G'_2G'_3 + G'_2G'_4 + G'_3G'_4$$

$$\frac{1}{K'_4K'_3K'_2} = \Sigma G'_1G'_2G'_3 = G'_1G'_2G'_3 + G'_1G'_2G'_4 + G'_2G'_3G'_4 + G'_1G'_3G'_4$$

$$\frac{1}{K'_4K'_3K'_2K'_1} = \Sigma G'_1G'_2G'_3G'_4 = G'_1G'_2G'_3G'_4$$

Expressing results in terms of classical constants necessitates the use of Equation 5, which is rather complicated. No substantial advantage is gained in doing this. It therefore appears advisable to express results directly in terms of titration constants and to abolish the classical constants altogether.

BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

THE ETHERATES OF MAGNESIUM BROMIDE

BY WARD V. EVANS AND HOWARD H. ROWLEY[1]

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The fact that the halides of magnesium are capable of uniting with ether to form compounds similar to hydrates has been known since the beginning of this century. Menschutkin[2] was the first to study them and gave them the name "etherates." He investigated their solubility in ether at various temperatures and found that as the solution became more concentrated, a heavy, oily, immiscible layer separated. He discovered that this heavy layer could be greatly supercooled and that when it did crystallize the magnesium halide was obtained in the form of the di-etherate. Later, Meisenheimer[3] and his co-workers discussed some of the properties of this oily liquid and of the crystalline magnesium halide etherates.

From a review of the literature, it is apparent that very little is known concerning the formulas of these etherates. Some claim that they contain one molecule of ether;[4] others, that they contain two molecules,[5] while some

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[1] University Fellow, 1927–1928.

[2] Menschutkin, *J. Russ. Phys.-Chem. Soc.*, 35,610 (1903).

[3] Jakob Meisenheimer and Johannes Casper, *Ber.*, 54B, 1655 (1921); Jakob Meisenheimer, Erich Piper and Hans Lange, *Z. anorg. allgem. Chem.*, 147,331 (1925).

[4] Tissier and Grignard, *Compt. rend.*, 132, 835 (1901); Grignard, *ibid.*, 136, 1262 (1903).

[5] (a) N. Zelinsky, *Chem. Zentr.*, II, 277 (1903); (b) W. Tschelinzeff, *Ber.*, 39, 773 (1906).

even claim that they contain three and four molecules[5a,b] of ether per molecule of magnesium halide. On the other hand, Ahrens and Stapler[6] claim that they obtained non-etherated magnesium halides precipitated from ether solution. It is also quite evident that little is known of the properties of these compounds.

Because of these conflicting statements, it was decided to make a study of the above-mentioned compounds using magnesium bromide as a typical magnesium halide.

Experimental Work

Preparation of Crystals.—Pure magnesium turnings were put into an Erlenmeyer flask and 100–200 cc. of dry ether added. All reasonable precautions were taken to eliminate air and moisture. Liquid bromine was then added, a few drops at a time, allowing the solution to clear considerably before the next addition was made. It was frequently advisable to cool the flask to keep the heat of reaction from boiling away the ether. Above a certain concentration (about 3% $MgBr_2$ at room temperature) two layers appeared, the upper one clear, colorless and of about the same density as ether, the bottom one a clear, heavy, oily liquid which usually ranged from very faint yellow to a reddish-brown. Only the faintly yellow layers crystallized but they gave beautiful crystals that seemed very pure. The crystals were prepared in two ways: (I) by separating the heavy bottom layer without contact with air or moisture and with a gentle suction removing part of the ether, leaving a supersaturated solution. Large crystals of magnesium bromide etherate were precipitated from the two layer system after standing for about one month. (II) By cooling the filtered two phase system below 10°, the heavy layer solidified forming white crystals. The clear liquid was decanted and the crystals drained. These crystals were much smaller than those prepared from the supersaturated solution but were easier to make and gave larger yields.

TABLE I

ANALYSIS OF CRYSTALS

Analysis	Method of prepn.	Method of analysis	Mg	Br	$(C_2H_5)_2O$
1	I	Loss of weight on heating in vacuum at room temp.	1	2	1.10
2	I	Same as No. 1	1	2	2.00
3	I	Loss of weight by vacuum	1	2	1.04
4	II	Same as No. 1	1	2	2.15
5	II	Same as No. 1	1	2	2.13
6	II	Same as No. 1	1	2	2.30
7	I	Loss of weight in vacuum	1	2	0.97
8	I	Same as No. 1	1	2	1.97
9	II	$Mg_2P_2O_2$ for Mg; AgBr for Br	1	1.95	2.68
10	II	AgBr for bromine	1	1.95	2.85
11	II	Same as No. 10	1	2	3.00
12	II	Same as No. 10	1	2	3.10
13	II	Same as No. 10	1	2	3.00

In analysis No. 1 the crystals were made at room temperature, dried in an atmosphere of ether, placed in a weighed test-tube fitted with a one-holed stopper carrying a

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[6] Felix B, Ahrens and Adolf Stapler, *Ber.*, **38**,3264 (1905).

short piece of glass tubing and weighed. The tube was then evacuated under 50-mm. pressure for twelve hours. It was then reweighed and the loss in ether recorded.

In analysis No. 2 the tube from analysis No. 1 was heated while being evacuated to constant weight. By comparing the last weight with the original weight, it was possible to determine the total weight of ether lost. It is seen that approximately one molecule of ether was lost quite easily by the first evacuation, while the total loss was two molecules, indicating that the crystals investigated contained two molecules of ether originally.

In analysis No. 3 the tube was left for forty hours at room temperature under a pressure of 50 mm. Since these crystals had been exposed for quite a time no effort was made to determine the total amount of ether lost but simply the amount left after the first evacuation.

In analyses Nos. 4, 5 and 6 the crystals were prepared by cooling the heavy layer and then drying the resulting crystals in a stream of carbon dioxide. Since there was no time limit to the passing of carbon dioxide over the crystals and since the tri-etherate has a very high vapor pressure, it is not surprising that these results vary and that they show values too high for a di-etherate and too low for a tri-etherate.

In analyses Nos. 7 and 8 large crystals were formed slowly at room temperature and broken up and the central portion was taken for analysis; hence these values should be quite accurate.

In analyses Nos. 9 and 10 the crystals were made at 0° and transferred to a weighed flask. The weighed crystals were dissolved in water, diluted and an aliquot part taken and analyzed. The results are low but indicate an etherate higher than the di-etherate.

In analyses Nos. 11, 12 and 13 the crystals were prepared at 0° but in a weighed flask. They were drained for one-half hour below 10°, weighed and analyzed. There was little chance for loss of ether due to exposure in these analyses.

From the results it seems clear that there are three definite etherates of magnesium bromide: (1) the tri-etherate which is readily decomposed, (2) the di-etherate which is more common, and (3) the mono-etherate. If the etherate is made at a temperature of about 0° and dried at this temperature and carefully analyzed, we obtain the tri-etherate. If the crystals are at all exposed, owing to their high vapor pressure we have a mixture of the di- and tri-etherates. If the crystals are made at room temperature we get the di-etherate, and if a tube containing the di-etherate is evacuated at room temperature under a pressure of 50 mm., we obtain the mono-etherate.

Analysis of Liquid Layers.—Menschutkin[2] made the statement that the concentration of the di-etherate in the two liquid layers varied with the temperature; therefore, it was decided to verify this. The two-layer systems were made in the usual manner and filtered through glass wool. The mixtures were then placed in flasks surrounded by water at a known temperature. Some of the bottom layer was then drawn into a dry pipet, allowed to run into a tared tube and weighed. The ether was then driven off by suction and heating until the weight of the residue was constant. Considering the residue as anhydrous magnesium bromide and the loss in weight as due to the ether, it was possible to calculate the ratio of ether in the bottom layer to the magnesium bromide.

TABLE II

ANALYSIS OF HEAVY LAYER

Analysis	Temp., °C.	Method of analysis	$MgBr_2$	$(C_2H_5)_2O$
1	11.2	Vacuum + heat	1	3.32
2	12	Vacuum + heat	1	3.48
3	14	Vacuum + heat	1	3.58
4	17	Vacuum + heat	1	3.40
5	17.5	Bromine as AgBr	1	3.46
6	19	Vacuum + heat	1	3.41
7	20	Vacuum + heat	1	3.59
8	20	Vacuum + heat	1	3.74
9	22.5	Vacuum + heat	1	3.51
10	22.5	Vacuum + heat	1	3.57
11	24	Mg by $Mg_2P_2O_7$; Br by AgBr	1	3.48
12	24	Vacuum + heat	1	3.45
		Average	1	3.50

Table II shows but slight change in concentration of the heavy oily layer with temperature. The irregularity of these results is due, no doubt, to the very slowly attained equilibria here involved. There is, however, a definite trend showing more ether in the solution at the higher temperature.

Table III shows a definite increase in magnesium bromide with temperature. The clear upper layer at room temperature always became cloudy and precipitated the heavy oily layer on cooling to a lower temperature. The amount of magnesium bromide in the upper layer at room temperature averaged about 3–3.5% and in the lower layer about 41%.

As to the composition of the top layer, there was very little work done. However, a few determinations were made by withdrawing five cubic centimeters with a pipet, putting it into a weighed crucible and treating with concentrated sulfuric acid. The ether was then burned off, the excess acid evaporated and the residue weighed as magnesium sulfate. From this, it was possible to determine the amount of magnesium bromide per 5 cc. of solution.

TABLE III

ANALYSIS OF TOP LAYER

Analysis	Temp., °C.	Method of analysis	Grams of $MgBr_2$/5 cc.
1	5	Mg as $MgSO_4$	0.0979
2	12	Same as No. 1	.1002
3	14	Same as No. 1	.1002
4	17	Same as No. 1	.1009
5	19.5	Same as No. 1	.1124
6	24	Same as No. 1	.1239
7	28	Same as No. 1	.1223
8	31	Same as No. 1	.1315

General Properties.—Some of the properties of the etherates mentioned in the literature were verified. The fact that the etherates were rather unstable and decomposed on contact with air and moisture, was brought out quite clearly by the analyses.

Action on Water.—The etherates are decomposed by water and ether is given off. Some experiments in which the volume of ether liberated from the di-etherate was measured indicated that one molecule of ether was displaced very readily but that the mono-etherate is more stable and requires a longer time for complete decomposition. This coincides with the work of Meisenheimer and Casper.[3]

Action of Absolute Alcohol.—When absolute alcohol was added to the crystals, ether was evolved as with water but not so vigorously.

Action of Dry Ether.—When ether was added to the di-etherate the crystals softened. When ether was added to the mono-etherate or the non-etherated magnesium bromide, there was a reaction and heat was given off, as was first noticed by Tschelinzeff.[5b]

Transition Points.—After it had been definitely shown that there are three distinct etherates, the next logical step was to determine the temperatures below which the various etherates are stable, that is, the points at which partial liquefaction takes place owing to the fact that ether is split off and the non-etherated or a lower etherated compound formed. Our work seemed to indicate that such points existed. The thermometric method failed; thus crystals prepared at 0° were heated slowly from 0 to 15° and the change in temperature plotted against time, but the curve showed no break. There did seem to be a change in the form of the crystals. The dilatometric method was also tried with no better result. This behavior can be explained on the ground that the equilibrium is very sluggishly attained and that the heat of formation of the etherate is rather low.

In spite of these negative results, experimental evidence strongly indicated a change in form of the crystals at about 13°. Crystals were prepared by cooling and then without decanting the excess liquid the crystals were maintained at some definite temperature for hours. By this method it was discovered that the crystals appeared to melt quite a bit below room temperature. Finally the value of 12.5° was reached, at which the crystals appeared stable. However, after about eight hours at this temperature (within 0.2°) the sharp outline of the crystals disappeared and a slow but nevertheless certain transformation of the crystals could be seen to be taking place.

Experiments were then conducted to approach the point from the other side. The two-layer mixtures were prepared and cooled to a definite constant temperature. They were then seeded with a crystal of the etherates. The temperature was raised each time until finally at 12.4° solidification took place very slowly. At 12.6' the heavy layer did not solidify when seeded. However, if this material stood for a month, crystals would grow in this layer as previously stated, but we considered them to be the di-etherate and not the tri-etherate.

Vapor Pressure Curves of Crystals.—If these etherates of magnesium bromide are definite compounds and have definite transition points, it should be possible to distinguish these points by means of their vapor pressures. It was decided that the static method of determination was best suited for this type of compound.

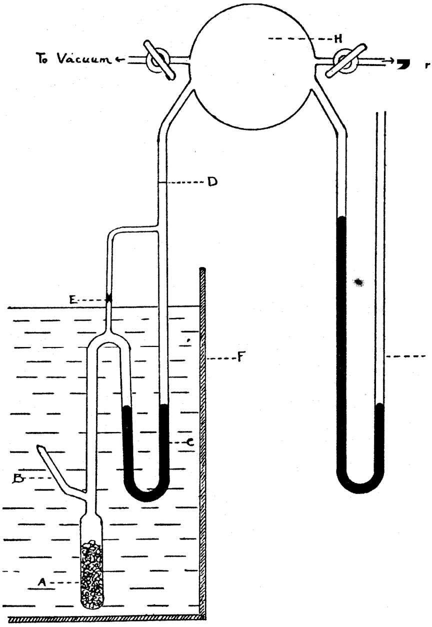


Fig. 1.—Apparatus for determining vapor pressure of crystals.

Apparatus.—Several types of apparatus were tried but due to the extreme ease with which the etherate crystals decomposed, it was found necessary to devise an apparatus in which the volume above the crystals was as small as possible. The apparatus in Fig. 1 was finally adopted as the most satisfactory. The entire apparatus with the exception of the bulb A was made from 8-mm. pyrex tubing. The bulb A and U-tube C were made separately for each determination and sealed to the permanent part at D. The bulb H was connected to the apparatus to give a larger volume and hence greater ease in regulating the height of the mercury in C. A commercial thermostat of standard make was used for all the determinations with this apparatus. The tenth of a degree thermometer used was compared to standard thermometers at frequent intervals.

Loading and Manipulation of Tensimeter.—The apparatus was washed with alcohol, then with ether, finally connected to the vacuum pump and heated with a blowtorch. The bulb A was then surrounded with ice and the crystals introduced through the side arm B, which was then sealed off. Mercury was placed in the U-tube C and the piece sealed to the rest of the apparatus at D. There was no water in the thermostat, the bulb A being surrounded with carbon dioxide snow. The apparatus was then connected to a vacuum oil pump which gave a vacuum of less than 1 mm. and the entire apparatus evacuated until the mercury ceased to rise in the manometer G. At the same time that the pressure became negligible (about one to two minutes), the connecting tube was sealed tight at E where a constriction had already been made. In this way the volume above the crystals was very small and at exactly the same temperature as the crystals themselves. Cold water was then run into the thermostat and as the vapor pressure of the crystals increased, air was let into the apparatus to equalize the levels of the mercury in the U-tube. If the vapor pressure decreased, air was drawn out.

Results.—After much experimenting at different temperatures, it was discovered that the temperature of the crystals at the time of evacuation was a very important factor. If the crystals were at 0° or even at $-10°$ the force of the pump was sufficient to decompose the tri-etherate and give lower values and inconsistent results. On the other hand, if the crystals were at the temperature of carbon dioxide snow, it was found that at this temperature the vapor pressure was only about 4 or 5 mm. and the crystals were not completely decomposed during the short time that the pump was in operation. On warming to a temperature of about 5°, the vapor pressure reached a value of about 233 mm., which is very close to the value for the vapor pressure of pure ether. The value, however, was a little low and reference to Fig. 2 will show how the variation increases with rise in temperature.

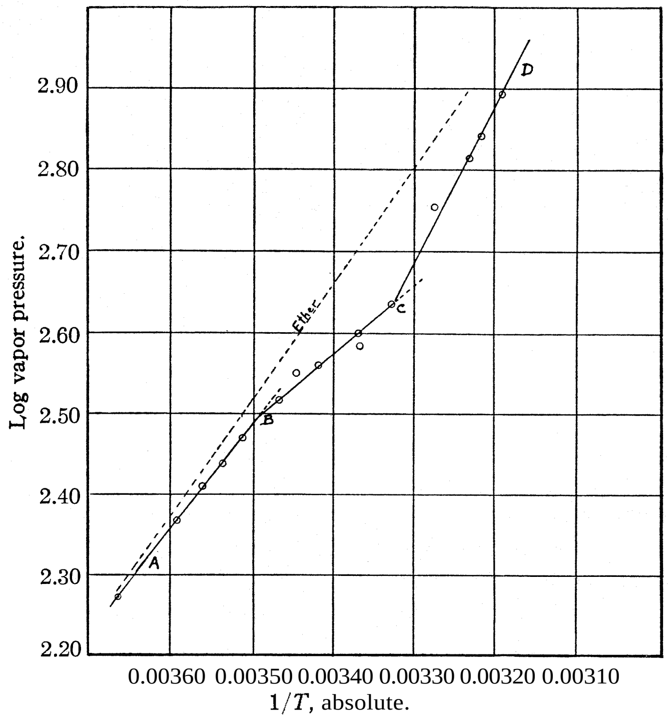


Fig. 2.—Vapor pressure curve starting with magnesium bromide tri-etherate at 5° and raising to 40°.

On raising the temperature of the crystals above 13°, they seemed to become soft with the appearance of some liquid. Above 30° they underwent a marked change with the formation of a large amount of liquid and a fine white precipitate. These changes were evident when the vapor pressure curves were drawn (Fig. 2).

TABLE IV

VAPOR PRESSURES STARTING WITH $MgBr_2 \cdot 3(C_2H_5)_2O$ AT 5° AND RAISING THE TEMPERATURE TO 40°

Temp. of bath, °C.	Barometer, mm.	Manometer, mm.	Vapor press., mm.	Log. V. P.	$1/T$ (abs.)
0.0	728.4	541	187.4	2.2728	0.003665
5.5	746	513	233	2.3674	.003590
7.9	751.5	494	257.5	2.4108	.003560
9.8	741	467	274	2.4378	.003536
11.8	747	452.5	294.5	2.4691	.003511
15 4	746	417.5	328.5	2.5165	.003468
17.3	742.5	387	355.5	2.5508	.003445
19.7	742	378.5	363.5	2.5605	.003416
23.9	737	353.5	383.5	2.5838	.003368
24.1	735.5	332.5	403	2.6053	.003366
27.2	735.5	308.5	427	2.6304	.003331
32.3	748	180	568	2.7544	.003275
36.3	746.5	93	653.5	2.8153	.003233
38.0	739	43	696	2.8426	.003215
40.4	738	+23.5	761.5	2.8817	.003191

In plotting the log of the vapor pressures against the inverse temperature (absolute), a straight line graph was produced (Fig. 2). This graph shows three distinct lines intersecting at two points (B and C). The first break in the curve occurs at 13.5°. The second break occurs at about 28°. Thus, the vapor pressure curves bear out the fact that three etherates of magnesium bromide exist: the tri-etherate, $MgBr_2 \cdot 3(C_2H_5)_2O$, stable below 13°; the di-etherate, $MgBr_2 \cdot 2(C_2H_5)_2O$, stable below 28°; and the mono-etherate, $MgBr_2(C_2H_5)_2O$, formed above 28°.

In reference to Fig. 2, it must be remembered that the lower curve AB is the vapor pressure curve for the system $MgBr_2 \cdot 3(C_2H_5)_2O$, $MgBr_2 \cdot 2(C_2H_5)_2O$, and ether vapor and at the transition point B we have the system $MgBr_2 \cdot 2(C_2H_5)_2O$, $MgBr_2 \cdot 3(C_2H_5)_2O$, solution and ether vapor. Thus, the next curve BC is the vapor pressure curve for $MgBr_2 \cdot 2(C_2H_5)_2O$, solution and ether vapor. In other words, it is the vapor pressure curve for a saturated solution of $MgBr_2 \cdot 2(C_2H_5)_2O$ in ether and not the curve for $MgBr_2 \cdot 2(C_2H_5)_2O$, $MgBr_2 \cdot (C_2H_5)_2O$ and ether vapor. At C, $MgBr_2 \cdot 2(C_2H_5)_2O$, $MgBr_2(C_2H_5)_2O$, solution and ether vapor are in equilibrium and the curve CD represented the system $MgBr_2(C_2H_5)_2O$, solution and ether vapor.

Since we have discovered that these systems reach equilibrium very slowly, it is only natural that if the temperature is raised suddenly, **the** solubility of $MgBr_2\cdot 2(C_2H_5)_2O$ in ether will increase, but if the solid dissolves very slowly to reach its equilibrium, the vapor pressure recorded will be the vapor pressure of an ether solution that is unsaturated with $MgBr_2\cdot 2(C_2H_5)_2O$ and since the vapor pressure decreases with concentration, this vapor pressure will be too high. On the other hand, if the temperature is lowered suddenly from an equilibrium at high temperature, we will have a solution supersaturated with respect to $MgBr_2\cdot 2(C_2H_5)_2O$ and hence a lower vapor pressure than we should have at this temperature. This would explain some of the difficulties encountered with the curves BC and CD in Fig. 2.

TABLE V

VAPOR PRESSURE OF $MgBr_2\cdot 2(C_2H_5)_2O$ SYSTEM

Temp. of bath, °C.	Barometer, mm.	Manometer, mm.	Vapor press., mm.	Log. V. P.	1/T (abs.)
0.0	735.6	689	46.5	1.6674	0.003665
5.0	742.5	669	73.5	1 8662	.003600
7.5	747.5	656	91.5	1.9614	.003565
8.5	751.5	650	101.5	2.0063	.003550
13.5	762	611	151	2.1790	.003490
18.5	760	536	224	2.3503	.003430
26.0	759	349	410	2.6128	.003344
28.0	742	284	458	2.6609	.003322
30.0	743	251	492	2.6919	,003300
31.0	743	229	514	2.7109	.003289

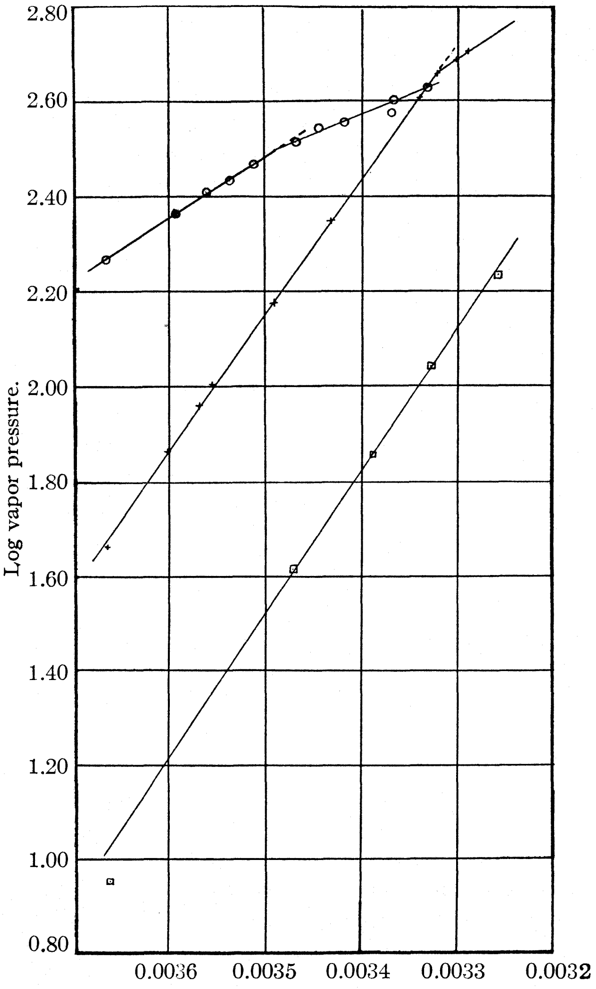
TABLE VI

VAPOR PRESSURE OF $MgBr_2\cdot(C_2H_5)_2O$ SYSTEM

Temp. of bath, °C.	Barometer, mm.	Manometer, mm.	Vapor press., mm.	Log. V. P.	1/T (abs.)
0.0	742	733	9	0.9542	0.003665
15.1	741	699.5	41.5	1.6180	.003471
22.1	742.5	670	72.5	1.8603	.003389
27.5	742.5	630.5	112	2.0492	.003328
34.1	739	566	173	2.2380	.003256

Figure 3 shows the vapor pressure curves of the three etherate crystals. Curve I is that of the tri-etherate, $MgBr_2\cdot 3(C_2H_5)_2O$, $MgBr_2\cdot 2(C_2H_5)_2O$ and ether vapor, showing the break at about 13°, where a solution of the di-etherate in ether is formed. Curve II is that of the di-etherate, $MgBr_2\cdot 2(C_2H_5)_2O$, mono-etherate and ether vapor, showing the point at about 28° where another molecule of ether is given off and a solution of the mono-etherate in ether is formed. The lower curve, III, is that of the mono-etherate crystals, $MgBr_2\cdot(C_2H_5)_2O$, $MgBr_2$ and ether vapor.

If these ether compounds of magnesium bromide are definite crystalline substances, it should be possible to obtain a "step" curve showing the vapor pressures of the different compounds at a constant temperature. A sample of the magnesium bromide–ether compound prepared by cooling the two-layer mixture, as previously described, was placed in a bulb connected to a manometer and fitted with a stopcock connected to a vacuum pump. The procedure consisted of drawing all the gas from the system with the pump, closing the stopcock and allowing the system to come to equilibrium. At first the bulb was immersed in a bath of solid carbon dioxide and acetone during the evacuation, which lasted for about one minute, in order to prevent the complete decomposition of the higher



○, Tri-etherate; +, di-etherate; □, mono-etherate.

Fig. 3.—Vapor pressure curves of etherate crystals of $MgBr_2$.

etherate before measurement could be taken. After closing the stopcock, this low temperature bath was replaced by ice and water, at which temperature the system was allowed to come to equilibrium. When all of the crystals had changed to the di-etherate, the time of evacuation was lengthened until some of the periods were for over an hour. During the latter part of the run the ice-bath was kept in place continually. Plotting vapor pressure of the crystals against the number of times evacuated, we

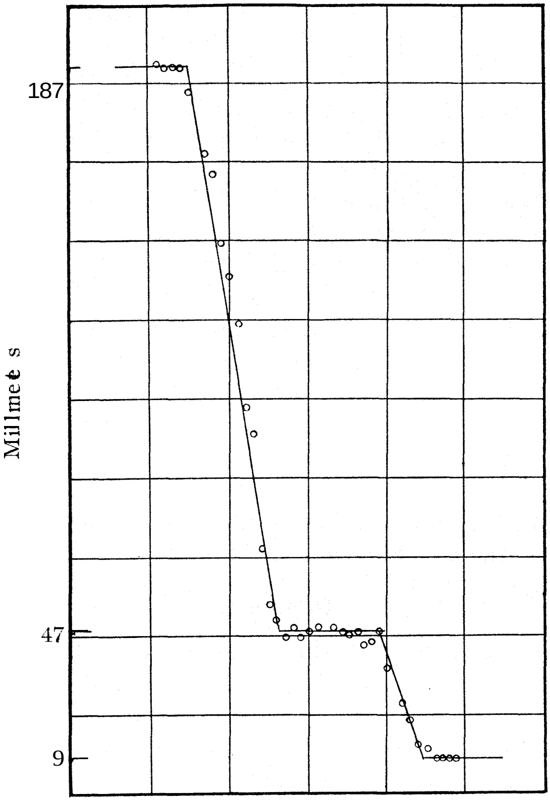


Fig. 4.—Vapor pressure of various etherates at 0°.

obtain a "step" curve as indicated in Fig. 4. The tri-etherate of magnesium bromide is shown with a pressure of 187 mm. at 0°. The pressure then drops to 47 mm., indicating a change to the di-etherate form. From this point it drops to 9 mm., which is the vapor pressure of the mono-etherate of magnesium bromide at 0°. This curve took about thirty days to complete due to slow equilibrium of the system.

Discussion

The most outstanding fact discovered in working with the etherate crystals of magnesium bromide is the slowness with which they change form. This was evident in all the experiments carried out in this Laboratory and was the reason why negative results were obtained in trying to determine the transition point of the crystals by means of the thermometric and dilatometric methods, even though there is quite a noticeable heat change in the transformation. No doubt this fact was also responsible for Menschutkin's statement that the crystals of the di-etherate of magnesium bromide melted at 22.8°.[2] He evidently prepared the crystals by cooling and then tried to determine the melting point in the usual way by slowly raising the temperature. As has been shown above, it is very easy to raise the temperature of the crystals to room temperature before they start to change form. In such a case it is not surprising that he obtained a value of 22.8"; a value, incidentally, which was not found in any of the work done in this Laboratory.

Because of the low transition point of the tri-etherate with extremely high vapor pressure and consequent unstability, it is not surprising that most of the workers reported the di-etherate as the only form, with an occasional mention of the mono-etherate. The principal fact that led to the exact identification of the tri-etherate was the break in the vapor pressure curve at 13°. If this break was the transition point of the di-etherate, it was extremely difficult to explain how it was possible to obtain the di-etherate crystals above this temperature. Thus, experiments were started to prove the existence of the third form with the success shown by the analyses. After the completion of this work, Meisenheimer[7] independently published an article stating the existence and some of the properties of this tri-etherate of magnesium bromide.

Summary

1. The existence of three distinct etherates of magnesium bromide has been shown.

2. Two transition points of the crystals were obtained, one where the tri-etherate changes to the di-etherate at 13 ± 0.5°, and the other where the di-etherate changes to the mono-etherate at 28 ± 1.0°.

3. Some of the properties of the etherates were studied with special reference to the slowness with which transition takes place.

4. The vapor pressures of the crystals were measured and the curves plotted.

EVANSTON, ILLINOIS

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[7] Jakob Meisenheimer, Ber., 61B, 708–20 (1928).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

A STUDY OF VAPOR PHASE OXIDATION OF ORGANIC COMPOUNDS, USING RARE EARTH OXIDES AS CATALYSTS.

I. METHYL AND ETHYL ALCOHOLS

BY FORD R. LOWDERMILK AND ALLAN R. DAY

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A large number of metallic oxides act as oxidation catalysts. In general this property can be explained by the fact that they are readily reduced to the metals or to lower oxides by the substances to be oxidized and are then re-oxidized by oxygen. This explanation seems to be adequate for certain oxides, such as the oxides of copper, nickel, cobalt, manganese, molybdenum, vanadium, etc. For certain other oxides, however, the mechanism is not quite so apparent, because, as far as is known, they are not readily reduced to lower oxides. For example, La_2O_3 and Y_2O_3 are active oxidation catalysts, but are not readily reduced.

A great many oxides have been used and with success in certain cases. A review of the literature indicated that even with the more commonly used catalysts there is still much work to be done, especially with regard to finer control and better methods for analyzing the products formed. In many cases the percentage of unoxidized material recovered is given, with no information concerning the method of recovery. In work of this nature where so many factors can influence the results, it is most important to choose analytical methods very carefully and only after thorough trial.

The oxidizing properties of cerium compounds have been known for a long time. In general for vapor phase oxidation at elevated temperatures they have been found to be too active, and the extent of the oxidation could not be easily controlled. The other elements of the rare earth group have not been studied. Apparently no work has been done with mixed catalysts, containing rare earth elements, for vapor phase oxidation.

The purpose of this investigation was two-fold: (1) to obtain quantitative data on the rare earth oxides as catalysts for vapor phase oxidation as compared with some less active catalyst such as copper oxide, and (2) to measure the effect produced by the addition of small amounts of rare earth oxides to some less active catalyst such as copper oxide.

After numerous preliminary experiments, samarium oxide was chosen because of its greater porosity. All of the members of the cerium group were tried and appeared to be equally active. Of the yttrium group only two, yttrium and lanthanum, were used in the preliminary work. They appeared to be less active oxidation catalysts and were much more apt to produce charring.

The preliminary work included oxidation of methyl alcohol, ethyl alcohol, ethylene, benzene and toluene. Some of the products qualitatively determined were not only interesting, but hold much promise for future work. Benzene, for example, yielded small amounts of phenol. Among the oxidation products of toluene, dibenzyl, benzaldehyde and benzoic acid were detected. Due to the greater ease of oxidation of methyl and ethyl alcohols, the rate of reaction, the temperature, etc., are more difficult to control. It was decided, therefore, to investigate carefully the oxidation of these alcohols first, with the hope that the data obtained would be useful in later experiments on the oxidation of substances not so readily oxidized.

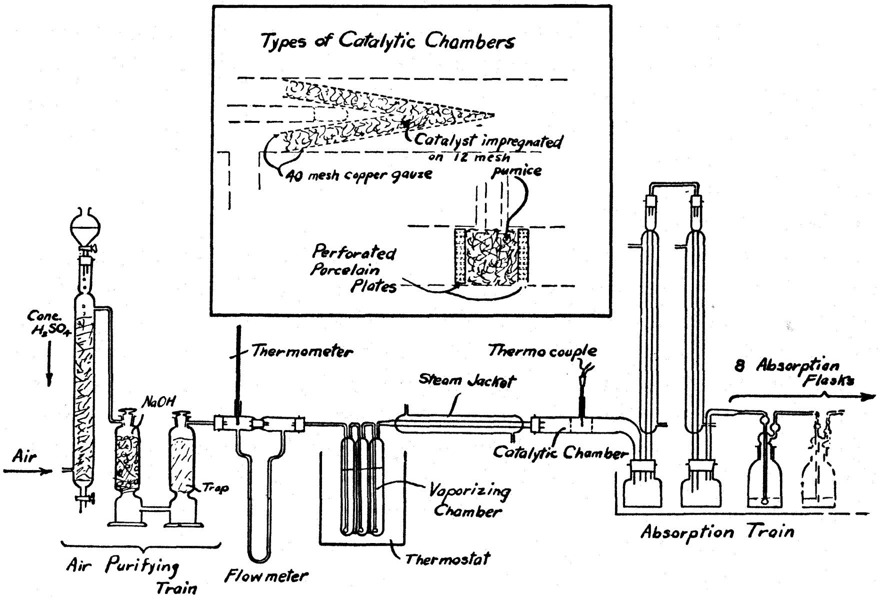

Fig. 1.—Apparatus.

The apparatus used is shown in Fig. 1. The arrangement of the apparatus was similar to that used by Le Blanc and Plaschke.[1] Dry air in definite amounts (as measured by a flowmeter) was passed through the alcohol contained in the vaporizing chamber. The outlet tube leading from the vaporizing chamber to the catalytic chamber was heated by means of a steam jacket to prevent condensation. The alcohol–air mixture was then passed over the catalyst in the pyrex catalytic chamber. The catalyst was supported (in the case of impregnated pumice) at each end by tightly fitting, finely perforated porcelain plates. The catalyst was 15 mm. in length and 17 mm. in diameter. In the cone type of catalyst two concentric cones of fine copper gauze were employed, the space between the cones being filled with catalyst impregnated upon pumice. The height of the outer cone was 60 mm., the diameter 20 mm. The diameter of the inner cone was 10 mm. The thickness of the pumice layer was 5 mm. Before the air–alcohol mixture was admitted to the catalytic chamber, the catalyst was heated to about 350° by means of a small burner. In all cases the heat of the reaction was sufficient to keep the catalyst at a red heat after the reaction had once started. The reaction temperatures were carefully measured by inserting a quartz thermometer or a

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[1] Le Blanc and Plaschke, *Z. Elektrochem.*, **17**, 45 (1911).

thermocouple in the side arm of the catalytic chamber. The thermocouple arm was protected by a quartz jacket. The end of the thermometer or thermocouple jacket was well buried at what appeared to be the hottest point. It is probable that the actual temperatures were somewhat higher than those recorded, since perfect contact with the catalyst was difficult to attain. The products of the reaction were collected in the cooling system and in the several absorption flasks. The receivers were then carefully emptied and rinsed, and the resulting solution diluted to a definite volume. Aliquots were taken for analysis, check analyses being made in all cases.

In most cases about 0.5 mole of alcohol was passed over the catalyst. In order to determine whether or not the yields varied with the amount of alcohol passed over, longer runs were made in which about 1.5 moles of alcohol was passed over. The yields of aldehyde in all cases checked very well with the yields obtained from the shorter runs. The amount of alcohol used for each run was simply determined by weighing the vaporizing chamber before and after each run.

The alcohols which were used were not perfectly anhydrous. As a result the vapors carried over by the air could not be considered to be purely aicohol vapors. This is a point which has been neglected by many previous investigators. It was found that the percentage of alcohol in the vapors passing over could easily be determined by making blank runs and determining the alcohol in the condensate by means of an immersion refractometer. That is, instead of passing the vapors over a heated catalyst, they were simply passed through an empty tube, condensed and the alcohol content determined as above.

Experimental

Oxidation of Methyl Alcohol

Constant boiling (65") methyl alcohol free from acetone was used. Three different catalysts were used: (1) pure Sm_2O_3 (prepared by heating samarium nitrate in a stream of oxygen at 450–500°); (2) pure CuO impregnated on 12-mesh pumice (prepared by dissolving 3 g. of CuO in nitric acid, to which solution was added 9 cc. of 12-mesh pumice and the mixture carefully evaporated to dryness with stirring; the dry pumice was then heated in oxygen as above); and (3) samarium and copper oxide mixtures on 12-mesh pumice (prepared similarly to the above).

The amounts of catalysts used have been given in the introduction. These figures represent the optimum amounts as carefully determined in the preliminary work.

The optimum bath or thermostat temperature was determined in preliminary experiments. Space does not permit recording all of the results of these experiments. Figure *2* shows that a bath temperature of 40° offers the best conditions (alcohol–air ratios) for obtaining the highest yields of formaldehyde.

Determination of Formaldehyde.—The aldehyde in the condensate was determined by the hydrogen peroxide–sodium hydroxide method.[2] This method gave excellent check results.

Determination of Unchanged Methyl Alcohol.—This was accomplished with satisfactory results by adding an excess of ammonium hydroxide to an aliquot of the condensate and distilling the solution. The distillate was just acidified with dilute sulfuric acid and then redistilled. The methyl alcohol content in this distillate was then determined by means of an immersion refractometer.

Use of Samarium Oxide as Catalyst.—Three to six cc. of 12-mesh oxide was used. The process yields of formaldehyde (1–5%) clearly indicated that this oxide was too active a catalyst. The catalyst temperature was always very high, never falling below 600°, even when a very low air rate was used. Even when the air supply was much less

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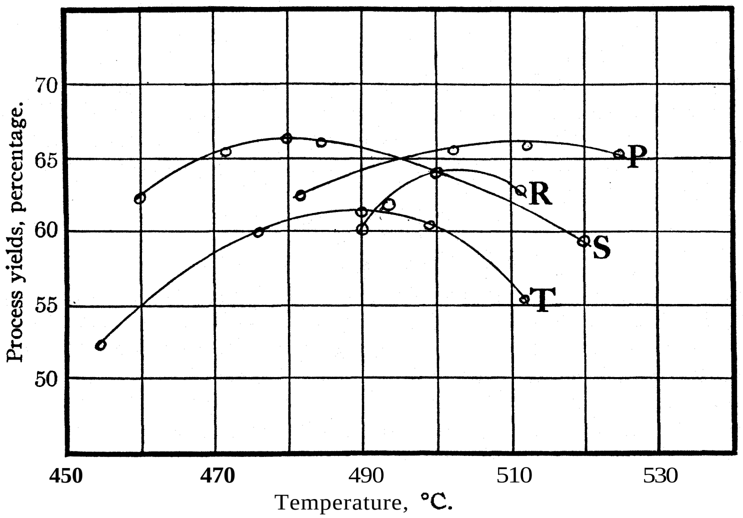
[2] Haywood and Smith, THIS JOURNAL, 27,1188 (1905).

than the amount theoretically necessary for the oxidation to formaldehyde, the yields were almost as small as before. This fact might be explained in either of two ways: (1) the oxidation does not stop with formaldehyde, but proceeds as far as carbon dioxide and water; or (2) formaldehyde is formed, but at the high temperature of the catalyst is immediately decomposed into hydrogen and carbon monoxide. That either explanation may be correct, depending upon the amount of oxygen used, was easily proved. A definite amount of absolute methyl alcohol was passed over the heated catalyst with almost the exact amount of oxygen (from air) necessary to oxidize the alcohol to formaldehyde. Of 26.97 g. of alcohol passed over, 6.4 g. was recovered. The difference between the two weights (20.57 g.) was oxidized. This amount of alcohol on oxidation to formaldehyde should yield 11.57 g. of water; actually 11.12 g. was formed. Further, it was found that fairly large amounts of hydrogen and carbon monoxide were formed but only traces of carbon dioxide. These facts seem to confirm the second explanation given above.



P, Bath at 37°; R, bath at 42°; S, bath at 40°; T, bath at 45°.

Fig. 2.—NOTE.—Due to the fact that a thermostat temperature of 40° permitted working at lower catalyst temperatures than a thermostat temperature of 37°, the former seemed to offer the more ideal conditions.

When an excess of oxygen is used, oxidation proceeds much further with the formation of larger and larger amounts of carbon dioxide and water.

It may be concluded, therefore, that the low yields of formaldehyde obtained even when insufficient oxygen was used were due to the catalytic decomposition of the aldehyde; and when an excess of oxygen was used the low yields were due primarily to a more complete combustion to carbon dioxide and water.

The results recorded in Table I represent mean results. The process yields were calculated on the basis of moles of methyl alcohol changed to moles of formaldehyde.

TABLE I

MEAN RESULTS (THERMOSTAT, 40°)

Catalyst	Air rate liters/min.	Oxygen ratio g. MeOH/l. O_2	Catalyst temp., °C.	Process yield, %
A. 3 g. CuO on 9 cc. pumice	1.08	1/0.296	484	63.5
	1.21	1/0.308	505	66.3
	1.30	1/0.310	515	66.5
	1.37	1/0.308	530	65.3
B. Sm_2O_3 (0.5%), CuO (99.5%), on pumice	1.08	1/0.308	494	63.4
	1 21	1/0.303	502	64.0
	1.30	1/0.308	515	64.5
	1.37	1/0.306	530	63.8
C. Sm_2O_3 (1%), CuO (99%), on pumice	1.08	1/0.309	485	58.5
	1.21	1/0.307	500	61.3
	1.30	1/0.299	513	63.7
	1.37	1/0.309	525	63 5
D. Sm_2O_3 (2%), CuO (98%), on pumice	1.08	1/0.300	473	53.5
	1.21	1/0.305	494	58.9
	1.30	1/0.309	505	59.3
	1.37	1/0.302	517	60 3
	1.58	1/0.309	532	61.1
	1.68	1/0.302	555	59 1
E. Sm_2O_3 (5%), CuO (95%), on pumice	1.21	1/0.307	506	37.6
	1.30	1/0.310	512	38.7
	1.50	1/0.306	532	40 8
	1.70	1/0.300	560	36.3

Discussion of Results

Preliminary experiments indicated that the best yields of formaldehyde were obtained at a thermostat temperature of 40° and when the alcohol–oxygen ratio was 1 g./0.3–0.31 liter of oxygen. The latter figures are somewhat below the theoretical values, as 0.35 liter of oxygen would be necessary to oxidize 1 g. of methanol completely to formaldehyde. The use of smaller or larger amounts of oxygen was accompanied by lower process yields of the aldehyde. The actual yields (based upon the actual amount of alcohol oxidized) varied inversely with the amount of oxygen used. It was possible to approach 100% actual yields when the amount of oxygen used was small. There was, of course, a corresponding decrease in the process yields, as more alcohol passed through unchanged, due to the lack of oxygen.

The alcohol–oxygen ratios recorded show the efficiency of the type of vaporizing chamber used. The constancy of these ratios certainly indicates that the air passing over the catalyst was saturated with respect to the alcohol regardless of the air rate used. This is a factor which, apparently, has been neglected in much of the previously published work.

Hofmann[3] first accomplished the formation of formaldehyde by passing

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[3] Hofmann. Ann., 145,357 (1868); Ber., 2,152 (1869); 11, 1686 (1878).

air laden with methyl alcohol over a heated platinum wire. Tollens[4] and Loew[5] improved the process by using copper gauze in place of platinum as a catalyst. Orloff[6] made the first careful investigation of the use of copper gauze. He reported about 50% as the highest process yield. Le Blanc and Plaschke[1] reported that silver gauze was a better catalyst than copper gauze, which fact has been confirmed by others. Fokin,[7] using asbestos impregnated with copper, reported a yield of 47%. Thomas,[8] using copper gauze as a catalyst, reported a maximum process yield of 63.6%. Bobrov[9] used copper gauze in the form of disks and reported an actual yield of 71.5%. From the published records Thomas has obtained the highest process yields.

The process yields given in Table I under A are somewhat higher than Thomas obtained when he used copper gauze. There is even a greater difference in the actual yields. Thomas reported an actual yield of 72% for the same run which gave a 63.6% process yield, whereas the actual yields using CuO on pumice in this investigation never dropped below 85%. This probably can be explained by the fact that his catalyst (copper gauze) was 74 mm. in length, while the catalyst layer (copper oxide on pumice) used in this investigation was only 15 mm. in length. Consequently, the products of the reaction escaped from the heated catalyst more quickly in the latter case with the result that a smaller percentage of aldehyde was decomposed.

All of the previous workers who used copper gauze as the catalyst have used a high air rate, generally two liters of air per minute. The best results obtained in this investigation were obtained at a much lower air rate, about 1.3 liters per minute. This rather curious difference must be due to the difference in the form of the catalyst. A comparison of copper gauze and pumice impregnated with copper oxide was made in the preparation of acetaldehyde (see Oxidation of Ethyl Alcohol).

It will be noted from the results recorded in Table I (B–E) that the introduction of small amounts of samarium oxide decreased the process yields, the decrease being very noticeable when the samarium oxide content reached 5%. The presence of the rare earth oxide had practically no effect on the catalyst temperatures. As the amount of samarium oxide increased, the yields became less and less, due to the decomposing action of this oxide on formaldehyde.

The actual yields also decreased with the introduction of Sm_2O_3, as shown by the following: A, 85–90%; B, 83–90%; C, 80–86%; D, 77–84% and E, 70–76%.

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[4] Tollens, *Ber.*, **15**, 1629 (1882); **16**, 917 (1883); **19**, 2134 (1886).

[5] Loew, *J. prakt. Chem.*, [2] **33**, 324 (1886).

[6] Orloff, *J. Russ. Phys.-Chem. Soc.*, **39**, 1023 (1907).

[7] Fokin, *ibid.*, **45**, 286 (1913).

[8] Thomas, THIS JOURNAL, **42**, 867 (1920).

[9] Bobrov, *J. soc. chim. russe, Industrie chimique*, **11**, 455 (1924).

The yields in Table I if plotted against catalyst temperatures would give curves showing a gradual rise in yields and then a gradual drop. Due to the ease of decomposition of formaldehyde, temperature control is undoubtedly the most important factor in its catalytic preparation. A second factor is the length of the catalyst. The preliminary work showed very definitely that the minimum amount of catalyst should be used. When more than this amount was taken, there was a very pronounced decrease in the process yields obtained,

Oxidation of Ethyl Alcohol

Pure ethyl alcohol (97%) free from aldehydes was used for the experiments. Three different catalysts were used: (1) pure samarium oxide; (2) (a) copper gauze in the shape of a cone—two cones were used as previously described, the space between was filled with 12-mesh pumice impregnated with copper oxide (Fig. 1)—(b) pure copper oxide impregnated on 12-mesh pumice and (3) (a) copper gauze cones as above—in this case the pumice layer between the cones was impregnated with samarium and copper oxide mixtures—(b) samarium and copper oxide mixtures impregnated upon 12-mesh pumice. The catalysts were prepared in the manner described under the oxidation of methyl alcohol.

The acidity of the various condensates was so slight that it could scarcely be explained on the basis of the presence of acetic acid. In greater part it was probably due to the presence of carbon dioxide. Ester formation was not noticed at any time during the course of the experiments.

Determination of Acetaldehyde.—The acetaldehyde in the condensate was determined by Ripper's method.[10] Check analyses were made and the results obtained usually agreed within 0.3–0.5%.

Determination of Unchanged Ethyl Alcohol.—The unchanged ethyl alcohol which was present in the condensate was much more difficult to determine. Several methods were investigated and finally the following was adopted. A suitable aliquot was taken, an excess of ammoniacal silver nitrate was added, and the resulting mixture was heated on a steam-bath under an efficient condenser for two to three hours, depending upon the amount of aldehyde present. The time may be shortened somewhat if the mixture is heated under a slight pressure. This effected the complete oxidation of the acetaldehyde in practically every case. The slightly ammoniacal mixture was distilled without filtration. The distillate was then just acidified with sulfuric acid and again distilled until about two-thirds of the solution passed over. The amount of alcohol in the distillate was determined by means of an immersion refractometer. This method proved quite satisfactory.

Use of Samarium Oxide as Catalyst.—Pumice (12-mesh) impregnated with samarium oxide was used as the catalyst. The results obtained were somewhat better than with methyl alcohol. The process yields varied from 6 to 15%. The oxide showed a great tendency to cause charring, and consequently the reactions were difficult to control. Charring was easily prevented by using an excess amount of air, but under those conditions combustion was practically complete.

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[10] Ripper, *Monatsh.*, 21, 1079 (1900); Feinberg, *Am. Chem. J.*, 49, 87 (1913).

Table II gives the average yields of acetaldehyde obtained using the various catalysts.

TABLE II

YIELDS OF ACETALDEHYDE (THERMOSTAT, 45°)

Catalyst	Air rate, l./min.	Oxygen ratio, g. EtOH/l. O_2	Catalyst temp., °C.	Process, yield, %
A. Copper cones, pumice layer impregnated with CuO	0.83	1/0.409	460	63.5
	.99	1/0.411	470	66.2
	1.08	1/0.421	481	68.4
	1.17	1/0.405	490	69.0
	1 22	1/0.418	500	68.7
	1.37	1/0.409	540	64.0
B. 3 g. CuO on 9 cc. pumice	0.59	1/0 430	429	65.4
	.71	1/0.417	482	70.5
	.83	1/0 422	501	68.8
	.88	1/0.417	512	66.2
	.99	1/0 417	532	64.4
	1.08	1/0.422	547	60.1
C. Copper cones, pumice layer impregnated with Sm_2O_3 (0.5%) and CuO (99.570)	0.71	1/0.409	446	62.8
	.88	1/0.405	478	69.5
	.99	1/0.412	485	68.3
	1.03	1/0.409	490	68.0
	1.08	1/0.420	493	67.3
	1.22	1/0.414	540	65.6
D. Sm_2O_3 (0.5%) and CuO (99.5%) on pumice	0.45	1/0.420	397	65.1
	.59	1/9.410	460	69.8
	.65	1/0.410	472	66.9
	.71	1/0.427	488	62.3
	.83	1/0.422	496	61.1
E. Copper cones, pumice layer impregnated with Sm_2O_3 (1%) and CuO (99%)	0.83	1/0.405	455	66.5
	.99	1/0.423	485	69.6
	1 03	1/0 417	505	68 5
	1.08	1/0.407	510	67.5
	1.22	1/0.405	525	63.5
F. Sm_2O_3 (1%) and CuO (99%) on pumice	0.45	1/0.427	400	65.6
	.59	1/0.418	465	67.4
	.71	1/0.425	495	63.5
	.83	1/0.420	525	58.8
	.99	1/0.410	555	55.4
G. Copper cones, pumice layer impregnated with Sm_2O_3 (2%) and CuO (98%)	0.83	1/0.410	430	65.6
	.94	1/0.422	500	66.2
	.99	1/0.404	505	68.0
	1.08	1/0.400	530	67.6
	1.22	1/0.420	550	63.2
H. Sm_2O_3 (2%) and CuO (98%) on pumice	0.45	1/0.420	395	67.5
	.59	1/0.410	435	65.8
	.71	1/0.412	485	60.3
	.83	1/0.417	512	57.5

TABLE II *(Concluded)*

Catalyst	Air rate, l./min.	Oxygen ratio, g. EtOH/l. O_2	Catalyst temp., °C.	Process, yield. %
I. Copper cones, pumice layer impregnated with Sm_2O_3 (5%) and CuO (95%)	0.71	1/0.401	410	57.0
	.83	1/0.422	435	58.9
	.99	1/0.400	460	63.4
	1 08	1/0.409	475	62.0
J. Sm_2O_3 (5%) and CuO (95%) on pumice	0.45	1/0.428	370	56.8
	.59	1/0.425	412	53.7
	.71	1/0.405	445	52.5

The catalyst could not be made to continue glowing at an air rate lower than 0.45 liter of air per minute.

Discussion of Results

Preliminary runs proved conclusively that the best results were obtained with a thermostat temperature of 45°. The results of these preliminary runs, when plotted against catalyst temperatures, gave curves similar to those under formaldehyde (see Fig. 2) with the curve for a thermostat temperature of 45° showing the best yields. Consequently, only the results obtained at the latter temperature are recorded here. The preliminary results plainly indicated that the optimum alcohol–oxygen ratio was 1 g. EtOH/0.40–0.43 liter of oxygen. The theoretical ratio is 1 g. EtOH/0.2434 liter of oxygen. The use of smaller or larger amounts of oxygen was always accompanied by a decreased process yield of acetaldehyde. However, as expected, the actual yields varied inversely with the amount of oxygen used. It was possible to approach 100% actual yields when a small enough quantity of oxygen was used; at the same time there was a corresponding decrease in the process yields. The ratios recorded under acetaldehyde again indicate the efficiency of the type of vaporizing chamber used.

As with methyl-alcohol, pure samarium oxide is too active a catalyst to be used for the oxidation of ethyl alcohol. It is not only apt to carry the oxidation too far, but it also probably catalyzes the decomposition of acetaldehyde similarly to formaldehyde.

Orloff[11] was the first to make a careful investigation of copper gauze as a catalyst for the oxidation of ethyl alcohol. He reported 66% as his best process yield.

Simington and Adkins[12] studied the catalytic oxidation of ethyl, isopropyl and n-butyl alcohols, using various catalysts. Using copper gauze they obtained only 37.4% process yield of acetaldehyde; using silver gauze they obtained 43.7%, and using a catalyst composed of 90% Cu and 10% Ag, they obtained 76% yields.

The results recorded in Table II (A and B) correspond more closely (for

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[11] Orloff, *J. Russ, Phys.-Chem. Soc.*, 40, 203 (1908).

[12] Simington and Adkins, THIS JOURNAL, 50, 1449 (1928).

copper gauze catalyst) to the results obtained by Orloff, although they are somewhat higher than his. Apparently the form of the catalyst has little effect on the yields, for the results under A and B are practically the same. One notable difference between them is evident from a comparison of the catalyst temperatures for the same air rates. For example, using an air rate of 0.83 l./minute, the catalyst temperature in A was 460°; in B, however, the temperature was 501°. This probably was due to the fact that the impregnated pumice offered a larger surface than the gauze. This would explain the fact that the best yields in B were obtained at lower air rates than those in A.

It will be noted from the results in Table II (C–J) that the introduction of small amounts of samarium oxide to the catalyst decreases the process yields, the decrease being especially noticeable when the samarium oxide content reached 5%. It will also be noted (B, D, F, H, J) that with the introduction of samarium oxide the optimum temperatures were materially lowered, *i. e.*, the best results were obtained from CuO on pumice at about 482°, with the catalyst containing 0.5% samarium oxide at 460°, with the catalyst containing 1% samarium oxide at 465°, with the catalyst containing 2% samarium oxide at 395° and with the catalyst containing 5% samarium oxide at 370°. This probably can be explained by the fact that with increasing amounts of samarium oxide the rate of decomposition of acetaldehyde, as well as the extent of oxidation, is increased and consequently best results are obtained at lower temperatures. Something not so easily explained, at present, is the fact that the temperatures measured for the 5% samarium oxide type of catalyst (for the same air rates) were lower than with pure CuO as catalyst, while with the catalysts containing 0.5% and 1% samarium oxide there was a noticeable temperature increase for the same air rates.

The introduction of samarium oxide also decreased the actual yields, as shown by the following: A and B, 76 to 89%; C and D, 76 to 86%; E and F, 75 to 85%; G and H, 75 to 81%; and I and J, 74 to 78%.

The points noted above were not so evident with the use of the double cone type of catalyst. Apparently the impregnated pumice layer was not so active, due to the fact that the copper gauze was effecting the greater part of the oxidation.

The results recorded in Table II, if plotted against catalyst temperatures, would give curves showing a gradual rise to the optimum temperature and then a fairly rapid drop. Certain workers have placed much stress upon the length of time the reacting gases were permitted to remain in contact with the catalyst (which, of course, depends upon the air rate and the length of catalyst layer). This is unquestionably an important factor, but in the case of methyl and ethyl alcohols it would seem that the catalyst temperature is the most important one as far as the yields are concerned.

Another important factor is the amount of catalyst used. In the case of copper gauze the length of the catalyst did not affect the results appreciably, but when impregnated pumice was used, the effect on the yields was quite evident. The use of too much catalyst produced a marked decrease in the yields of acetaldehyde.

Conclusions

The results obtained in this investigation indicated that the presence of rare earth oxides with copper oxide promoted oxidation. With such easily oxidizable substances as methyl and ethyl alcohols this fact was of no apparent advantage, since the oxidation tends to go too far. This enhanced activity should prove to be very advantageous in the oxidation of less readily oxidizable substances. Work has been started along these lines.

It is believed that the presence of rare earth oxides, in small amounts, helps to prevent catalyst poisoning and prolong the life of the catalyst indefinitely. Actual proof has not yet been obtained. Work is being started with rare earth oxides and silver oxide mixtures and it is hoped that this latter point can thus be easily proved.

Summary

1. Data have been obtained on the use of rare earth oxides for the vapor phase oxidation of methyl alcohol and ethyl alcohol, as compared with the results obtained when copper oxide was used for the same purpose.

2. Better yields of formaldehyde and acetaldehyde have been obtained, using pumice impregnated with copper oxide, than have been reported previously by investigators who used some form of copper as the oxidation catalyst.

3. Data have been obtained showing the effect produced on the catalytic activity of copper oxide by the addition of small amounts of rare earth oxides to the copper oxide.

PNILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS. X. THE POLARIZATION AND REFRACTION OF THE NORMAL PARAFFINS

BY R. W. DORNTE AND C. P. SMYTH

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This investigation was undertaken with the object of obtaining further information concerning the temperature dependence or independence of the polarization of substances possessing little or no electric moment and of studying the variation of this polarization in an homologous series. Through the kindness of the Ethyl Gasoline Corporation it has been possible to obtain samples of the straight-chain hydrocarbons from pentane to dodecane prepared by Dr. Albert L. Henne of Ohio State University, to whom the writers wish to express their indebtedness. The samples of these liquids were of a high degree of purity boiling over a range of only 0.02 to 0.03°. Although the densities and refractive indices of these substances had been measured previously, the measurements were repeated in order that all the data used should have been determined for the same materials, these materials being of exceptional purity. Moreover, the previous density measurements did not extend over the wide range of temperature which it seemed desirable to employ in the polarization investigations. Wherever the present results overlap data given in "International Critical Tables" excellent agreement is obtained.

In the first of this series of papers[1] the method of obtaining the electric moment of the molecule of a substance has been discussed. The molar polarization of a substance, $P = (\epsilon - 1)/(\epsilon + 2) \times M/d = P_E + P_A + P_M$, in which ϵ is the dielectric constant, M is the molecular weight, d is the density, $P_E + P_A$ is the polarization due to shifts of charges in the molecule inducible by an external field and P_M is the polarization due to the orientation of the permanent electric doublets of the molecules. When P_M is 0, the moment of the molecule must be 0. P_E may be calculated as the molar refraction for light of infinite wave length, MR, $= (1 - \lambda_0^2/\lambda^2)[(n^2 - 1)/(n^2 + 2) \times M/d]$, where n is the index of refraction for light of wave length λ and λ_0 is the wave length corresponding to a characteristic vibration frequency in the ultraviolet region. P_A, the difference between P_E, the polarization due to electronic shifts and the total induced polarization, is commonly attributed to induced shifts of atoms or radicals. The variation of P with the absolute temperature T is shown by the equation, $P = a + b/T$, in which the constant $a = P_E + P_A$, $b/t = P_M$, and the constant $b = 4\pi N\mu^2/9k$, where μ is the electric moment of a single molecule, N is the number of molecules in a gram molecule $= 6.061 \times 10^{23}$, and k is the molecular gas constant $= 1.372 \times 10^{-16}$. Evidently, if P does not

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[1] Smyth, Morgan and Boyce, THIS JOURNAL, 50, 1536 (1928).

change with changing temperature, it is to be concluded that b is zero and that therefore the moment of the molecule is zero. If the molecule possesses a moment, P should decrease with rising temperature.

The refractive indices were measured with a Pulfrich refractomcter and the molar refractions MR and dispersions calculated in the manner described in the third paper of this series.[2] The densities and dielectric constants were measured with the apparatus described in earlier papers,[1,3] the only modification being the insertion of two stages of amplification in the detector circuit of the capacity bridge. The dielectric constant of the benzene used in calibrating the condenser was taken as 2.2176 at 25". Both the dielectric constants and densities were measured at definite temperature intervals of 20" by adjusting the constant temperature bath to the exact temperatures shown in the following tables, the temperature being held constant to ±0.05° below 0° and above 90° and to ±0.02° at the intermediate temperatures. The experimental data and the polarizations and refractions calculated from them are given in Tables I and II, and in Fig. 1 the values of the polarization are plotted as ordinates against those of the temperature as abscissas. In order to keep the diagram within reasonable dimensions, the ordinates are broken several times, but the same scale is maintained throughout.

TABLE I

REFRACTIVE INDICES AND MOLAR REFRACTIONS AT 20°C.

	n_γ	n_β	n_D	n_α	MR_γ	MR_β	MR_D	MR_α
Pentane	1.36600	1.36267	1.35801	1.35663	25.79	25 57	25.28	25.19
Hexane	1.38318	1.37951	1.37490	137308	30 45	30.19	29.86	29.73
Heptane	1.39636	1.39251	1 38777	1 38584	35.19	34.89	34 51	34.36
Octane	1.40652	140238	1.39755	1.39559	39.91	39.55	39.13	38 96
Nonane	1.41458	1.41043	1.40550	1.40351	44.65	44.22	43.78	43.60
Decane	1.42119	1.41691	1.41192	1.40982	49.36	48.92	48.41	48.19
Undecane	1.42656	1.42239	1.41730	1.41519	54.10	63.53	53.06	52.83
Dodecane	1.43094	1 42685	1 42170	1.41959	58 77	58 30	57.67	57.42

TABLE II

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS

I, °C.	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}	$C_{10}H_{72}$	$C_{11}H_{24}$	$C_{12}H_{26}$
				Dielectric Constants				
−90	2 011	2 044	2 073	.....	.....	.....	.....	.....
−70	1.984	2017	2.047	.....	.....	.....	.....	.....
−50	1.955	1.990	2.021	2.037	2.059	.....	.....	.....
−30	1.924	1.963	1995	2.013	2035	2050	.....	.....
−10	1892	1.936	1.968	1.987	2.010	2.027	2.039	2.047
10	1.860	1.906	1.940	1.961	1.985	2.003	2.017	2025
30	1.828	1.875	1.912	1.935	1.959	1.979	1994	2.002
50	.....	1.844	1.881	1.907	1.932	1.954	1.969	1.978

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[2] Smyth and Stoops, THIS JOURNAL, 50, 1883 (1928).

[3] Smyth and Morgan, *ibid.*, 50, 1547 (1928).

TABLE II (Concluded)

t, °C.	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$	$C_{11}H_{24}$	$C_{12}H_{26}$
70	.....	.....	1.849	1.879	1.905	1.928	1.944	1.954
90	.....	.....	1.815	1.849	1.878	1.901	1.918	1.930
110	.....	.....	.....	1.817	1.847	1.873	1.893	1.906
130	.....	.....	.....	.....	1.818	1.844	1.866	1.881
150	.....	.....	.....	.....	1.787	1.814	1.838	1.856
170	.....	.....	.....	.....	.....	1.783	1.810	1.830
190	.....	.....	.....	.....	.....	.....	1.781	1.803
210	.....	.....	.....	.....	.....			1.776

Densities

t, °C.	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$	$C_{11}H_{24}$	$C_{12}H_{26}$
−90	0.7257	0.7533	0.7738	.....	.....			
−70	.7083	.7370	.7580	.....	.....	.....	.....	.....
−50	.6908	.7206	.7420	0.7588	0.7726	.....	.....	.....
−30	.6728	.7037	.7256	.7432	.7573	0.7687	.....	.....
−10	.6545	.6869	.7092	.7275	.7417	.7538	0.7630	0.7715
10	.6359	.6692	.6927	.7114	.7260	.7385	.7482	.7571
30	.6163	.6507	.6755	.6945	.7105	.7230	.7333	.7424
50	.....	.6318	.6577	.6781	.6945	.7075	.7182	.7274
70	.....	.....	.6395	.6610	.6776	.6916	.7027	.7125
90	.....	.....	.6210	.6437	.6616	.6754	.6875	.6974
110	.....	.....	.....	.6257	.6445	.6583	.6720	.6820
130	.....	.....	.....	.....	.6272	.6421	.6563	.6665
150	.....	.....	.....	.....	.6096	.6257	.6398	.6509
170	.....	.....	.....	.....	.....	.6088	.6224	.6345
190	.....	.....	.....	.....	.....	.....	.6038	.6170
210	.....	.....	.....	.....	.....	.....	.....	.5986

Polarizations

t, °C.	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$	$C_{11}H_{24}$	$C_{12}H_{26}$
−90	25.04	29.51	34.09	.....	.....	.....	.....	.....
−70	25.14	29.58	34.17	.....	.....			
−50	25.20	29.65	34.26	38 64	43.28	.....		
−30	25.23	29.74	34.37	38.77	43.41	47.95	.....	.....
−10	25.25	29.81	34.44	38.84	43.53	48.10	52.66	57.07
10	25.26	29.85	34.48	3893	43.63	48.24	52.85	57.25
30	25.30	29.88	34.55	39.05	43.69	48.38	53.01	57.40
50	.....	29.92	34.56	39.08	43.74	48.48	53.09	57.53
70	.....	.....	34.53	39.13	43.83	48.57	53.20	57.64
90	.....	.....	3444	39.11	43.85	48.62	53.23	57.75
110	.....	.....	.....	39.05	43.78	48.68	53.31	57.89
130	.....	.....	.....	.....	43.77	48.62	53.31	57.97
150	.....	.....	.....	.....	43.69	48.49	53.30	58.05
170	.....	.....	.....	.....	.....	48.33	53.35	58.13
190	.....	.....	.....	.....	.....		53.43	58.25
210	.....	.....	.....	.....	.....			58.43

In Fig. 1 the scale on which the polarization is plotted is so large that several of the points appear to lie at some distance from the straight lines drawn to represent them. The values for heptane. octane. nonane and decane show an increasing tendency to fall below the straight lines as the boiling point is approached. This deviation from linearity is regular and greater than the probable experimental error, but, as it is not apparent in the pentane, hexane, undecane and dodecane values, for which the same experimental technique was used and to which the same theoretical considerations should apply, its cause must be regarded as obscure and, possibly, accidental. The results indicate, however, that, as in the case of the isomers of heptane[2] previously investigated, the polarization varies but little with temperature, the variation being an approximately linear increase with rising temperature instead of the hyperbolic decrease required by the equation for the temperature variation of the polarization of substances possessing a moment. Cases have been found[3,4] in which pure substances possessing large moments show a rise in polarization with rising temperature instead of the expected fall because the rising temperature decreases the intermolecular action or association which is reducing the

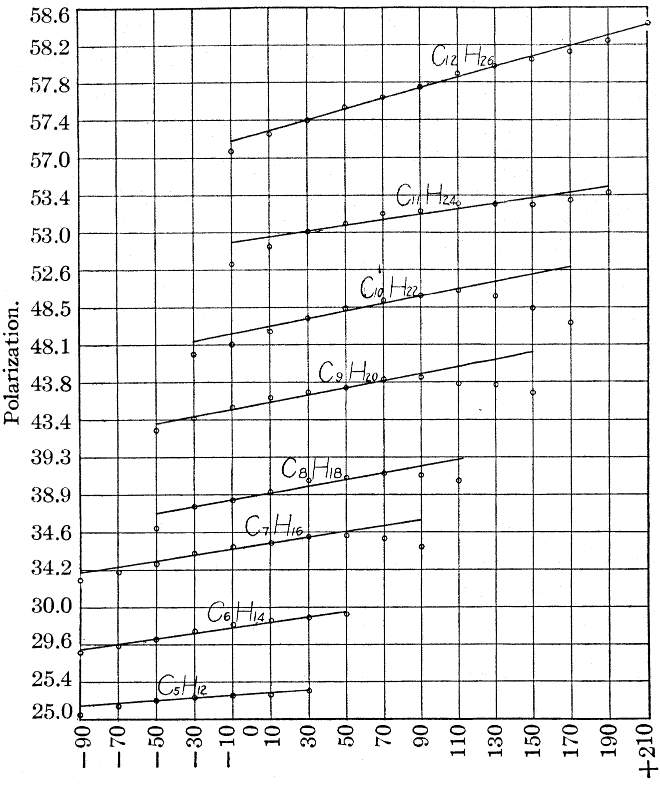

Fig. 1.—Variation of polarization with temperature.

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[4] Smyth and Stoops, THIS JOURNAL, 51, 3312, 3330 (1929).

polarization. In these cases, the polarization, in spite of its reduction by intermolecular action, has been found to be considerably larger than the molar refraction, but the polarizations of these hydrocarbons at 20° are almost identical with the refractions for the sodium D line at this temperature. Only when the refraction is extrapolated to infinite wave length to obtain the values shown under P_E in Table III is the difference between P and P_E appreciable. The difference $P - P_E$ is smaller than the values commonly found for P_A,[5] which indicates a very small, if not zero, value for P_M as $P - P_E = P_A + P_M$. Moreover, the increase in $P - P_E$ in going up the series from pentane to dodecane is less than that commonly observed for P_A with increase in molecular weight, which indicates a negligible variation in any possibly existing moment. As the temperature variation of P also points to a small, if not zero, value for P_M, it may be concluded that the values of P_M and, hence, of the electric moments of the molecules, are indistinguishable from zero by the experimental method which has been employed. The difference $P - P_E$ is, therefore, set equal to P_A to obtain the values listed in Table III along with the dispersions and the values at 20° of the other constants which have been discussed.

TABLE III

PHYSICAL CONSTANTS AT 20°C.

		d	P	P_E	P_A	$MR_\gamma - MR_\alpha$	$n_\gamma - n_\alpha$
Pentane	1.845	0.6263	25.30	24.69	0.61	0.60	0.00937
Hexane	1.890	.6600	29.85	29.18	.67	.72	.01010
Heptane	1.926	.6842	34.51	33.74	.77	.87	.01052
Octane	1.950	.7033	39.03	38.25	.78	.95	.01093
Nonane	1.972	.7182	43.66	42.88	.78	1.05	.01107
Decane	1.991	.7306	48.32	47.36	.96	1.17	.01127
Undecane	2.005	.7406	52.92	51.89	1.03	1.27	.01137
Dodecane	2.017	.7495	57.49	56.38	1.11	1.35	.01135

The value of P_A for heptane in Table III is smaller than that found by Smyth and Stoops by 0.11, which, in view of the lower value, 2.276, instead of 2.279, assigned to the dielectric constant of benzene used as standard in the calibration of the apparatus, may be regarded as excellent agreement. The values increase with increasing molecular weight in a manner to be expected from the increase in P and P_E. In view of the absence of moment, it is interesting to see whether the polarization resembles the refraction in being an additive property, as might be expected. For this purpose, the differences between the refractions and also the polarizations of successive members of the series are shown in Table IV, the difference in each case being the contribution of a CH_2 group.

The mean values of the refractions for the CH_2 group at different wave lengths agree well with those given in Landolt-Börnstein (5th ed.), which

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[5] Smyth, THIS JOURNAL, 51, 2051 (1929).

TABLE IV

REFRACTION AND POLARIZATION OF CH_2 GROUP

	MR_γ	MR_β	MR_D	MR_α	P_E	P
C_6H_{14} C_5H_{12}	4.66	4.62	4.58	4.54	4.49	4.55
C_7H_{16}–C_6H_{14}	4.74	4.70	4.65	4.63	4.56	4.66
C_8H_{18}–C_7H_{16}	4.72	4.66	4.62	4.60	4.51	4.52
C_9H_{20}–C_8H_{18}	4.74	4.67	4.65	4.64	4.63	4.63
$C_{10}H_{22}$–C_9H_{20}	4.71	4.70	4.63	4.59	4.48	4.66
$C_{11}H_{24}$–$C_{10}H_{22}$	4.74	4.71	4.65	4.64	4.53	4.60
$C_{12}H_{26}$–$C_{11}H_{24}$	4.67	4.67	4.61	4.59	4.49	4.57
Mean value	4.711	4.676	4.627	4.604	4.527	4.60
Landolt–Börnstein	4.710	4.668	4.618	4.598		

are shown at the bottom of the table. In going down the columns of both the refractions and the polarizations there is a slight alternation in the values for the CH2 group, which suggests the possibility that the refraction and polarization of a molecule with an even number of carbon atoms in an unbranched chain may be proportionately a little lower than those of a molecule with an odd number of carbons in the chain. The range within which the values of P vary is slightly greater than that within which those for the more accurately measurable MK,, MR_β, MR_D and MR_α vary but no greater than the range of the value of P_E, in which the errors of measurement accumulate. As the values of P vary about the figure **4.60** without any trend upward or downward it is evident that the polarization of these hydrocarbons is an additive property, although a glance at the values of the dielectric constants in Table III shows that this quantity is decidedly not an additive property. The difference of the mean values of P and P_E for the CH2 group gives a value **0.07** for P_A for this group, which cannot, however, be regarded as of general significance.

The increase of polarization with temperature, about 1% per 100° in the absence of the depression noted for some substances as the boiling point is approached, is of the same magnitude as that found previously for *n*-heptane and two of its isomers. It was suggested in this work[4] that the force fields of adjacent molecules might reduce the mobilities of the bound electrons to a small extent, thereby reducing the polarization and refraction and that, as the molecular separation and motion increased with rising temperature, the effect of the force fields upon the electrons was decreased, the polarization and refraction thus being increased. However, subsequent investigations of the refractions of mixtures of heptane with strongly polar molecules,[6] including ethyl and butyl alcohol, have shown that the refraction of the mixture is a linear function of composition, deviations from linearity being of the magnitude of the experimental error, about **0.02** units. The very different force field around the heptane molecule when it is surrounded with alcohol molecules instead of with other heptane molecules

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

might be expected to bring about a considerable change in the refraction and polarization if the change of polarization with temperature observed in the present work were due to change in the effect of the molecular force fields. The absence of any such considerable change of refraction with concentration would, therefore, seem to argue strongly against the attribution of the increase of polarization with temperature to decreasing effect of the force fields. It was also suggested that a more important factor might be the increase in the number of degrees of freedom with increasing temperature, which should facilitate the displacement of charges in the molecule and, hence, increase the polarization. It must, however, be borne in mind that, in the derivation of the expression for refraction and polarization, factors have, of necessity, been neglected, the effects of which may be negligible in comparison to that of a large dipole moment, but which, in the absence of **a** moment, may easily become evident in the results of careful measurements.

The zero or exceedingly small moments of the molecules of these hydrocarbons, as in the case of the isomers of heptane, show the absence of any polarity in the bonds of alkyl radicals which may be detected through the electric moments arising from them, and, consequently, give no evidence of a difference in the electronegativities of the radicals.

Summary

The dielectric constants and densities of the normal paraffins from pentane to dodecane have been measured over almost the entire temperature range within which these substances are liquid at atmospheric pressure and the refractive indices and dispersions have been determined at 20°.

The polarizations calculated from the dielectric constants and densities increase about 1% per 100° rise in temperature. The molar refractions at different wave lengths obtained for the CH_2 group agree well with those in the literature and the constancy of the polarization of the CH_2 groups show that, in the absence of an electric moment, the polarization is an additive property, as would be expected.

The absence of any decrease of polarization with rising temperature and the small difference between the polarizations and the refractions show that the values of the electric moments of the molecules are indistinguishable from zero. The moments are, therefore, regarded as approximately zero and the conclusion is drawn that the bonds of alkyl radicals possess no polarity detectable through electric moments arising from them.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. XXXV. GERMANIUM MONOXIDE. GERMANIUM MONOSULFIDE[1]

BY L. M. DENNIS AND R. E. HULSE

RECEIVED JUNE 9, 1930 PUBLISHED SEPTEMBER 5, 1930

Germanium Monoxide

Indications of the existence of this compound were observed by Winkler[2] but he was unable to purify the product for analysis. Consequently his statement that it is germanous oxide lacked experimental confirmation. Isolated details have since then appeared in the literature,[3] but none of the investigators made a systematic study of the compound. To extend our knowledge of this substance and possibly to open the way to the general study of the compounds of divalent germanium, about which comparatively little is known at present, this investigation was taken up.

Experimental

Preparation of Hydrous[4] Germanium Monoxide.—Germanium dioxide was dissolved in a slight excess of a 5 N solution of potassium hydroxide, hydrochloric acid was added in amount necessary to make the solution about 5 N in respect to HCl,[5] an excess of a 30% solution of hypophosphorous acid was then added, and the solution was held at 95° for two hours.

Since the hydrous germanium monoxide is quickly oxidized by air, it was necessary to precipitate and wash the compound in an inert atmosphere. This was accomplished with the apparatus shown in Fig. 1.

The reduced solution was placed in the cylinder A which was surrounded by a jacket through which hot water was kept circulating. Through the rubber stopper in the top of A were inserted a tube carrying a small separatory funnel and a branch M, a glass hand-stirrer B which passed loosely through a short piece of glass tubing, and a siphon tube D.

The air above the solution in A was displaced by hydrogen which entered through M and escaped around the glass rod B. This passage of hydrogen was continued throughout the operation.

Germanous hydroxide was now precipitated by adding dilute ammonium hydroxide through C. The contents of A was then held at about 90° for one hour by the hot water rising from the flask and filling the jacket around A. The precipitate was then allowed

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[1] This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by R. E. Hulse in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Winkler, *J. prakt. Chem.*, 142, 177 (1886).

[3] Biltz, *Z. anorg. Chem.*, 72, 313 (1911); Dennis, *ibid.*, 174, 107 (1928); Hantzsch, *ibid.*, 30, 289 (1902); Bardet and Tchakirian, *Compt. rend.*, 186, 637 (1928).

[4] This term was introduced by Weiser to distinguish precipitated oxides that contain varying amounts of water, from hydrates in which water is chemically combined in definite stoichiometric proportions. See Weiser, "The Hydrous Oxides," 1926.

[5] When the solution is acidified, some germanium dioxide is precipitated, but this dissolves during the reduction.

to settle, the supernatant liquid was drawn off through D, hot water that had been boiled to free it from air was run in through C, and the mixture was stirred by moving B up and down and turning it. The precipitate was again allowed to settle, the supernatant liquid was drawn off, and the operations of washing were repeated until most of the soluble salts had been removed, which was shown by the tendency of the precipitate to become colloidal. Precipitate and liquid were then run into F by opening E and the precipitate was collected on a filter paper in the Biichner funnel G. Contact with the air was here avoided by surrounding G with the glass cylinder F which was closed at top and bottom with large rubber stoppers. The precipitate was washed until free from chloride, and was then quickly transferred to a boat of porcelain or alundum. This was inserted into a combustion tube and the precipitate was dried by heating it in a current of pure nitrogen to the desired temperature.

Freshly precipitated hydrous germanium monoxide varies in color from yellow to red, depending upon the conditions of precipitation. It is readily soluble in the halogen acids. Sulfuric acid, 6 N, changes its color to dark brown (partial dehydration) and slowly dissolves it. It is only slightly soluble in fixed alkalies, but forms red colloidal solutions.

When dried by heating in *vacuo*, water was steadily removed, and no evidence of the formation of definite hydrates was obtained. As the temperature of drying is raised, the oxide changes in color from red to brown to black, with decrease in solubility. Examination under the microscope showed that the particle size increases as the color becomes darker, which indicates that the color change is not due to tautomerism as Hantzsch supposed, but is dependent upon the size of the particles and the amount of water associated with the oxide.

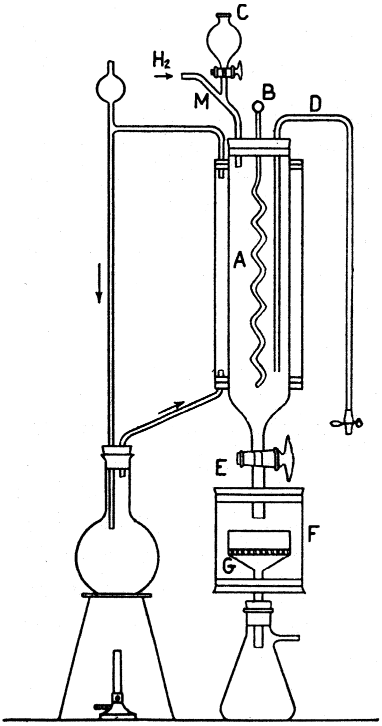

Fig. 1.

Anhydrous Germanium Monoxide.—Hydrous germanium monoxide is completely dehydrated when heated in nitrogen to 650°, and jet-black crystalline germanium monoxide, GeO, results. It was analyzed by oxidizing it with pure hydrogen peroxide, evaporating the solution to dryness, heating the residue to 800° and weighing the resulting GeO_2.

Anal. Subs., 0.1401, 0.1515. Calcd. for GeO: Ge, 0.1143, 0.1248 = 81.94%. Found: Ge, 0.1147 = 81.87%, 0.1240 = 81.81%.

Properties.—Anhydrous germanium monoxide is not acted upon by moisture or atmospheric oxygen at room temperature, is attacked very slightly, if at all, by hydrochloric or sulfuric acid or solutions of fixed alkali hydroxides, but is slowly oxidized by fuming nitric acid, potassium permanganate or chlorine water. It is rather readily oxidized by hydrogen peroxide in the presence of ammonium hydroxide. Oxidation in dry air begins at 550°. When heated in a closed apparatus in pure nitrogen, the oxide sublimes at 710°.

When heated in nitrogen in a boat of platinum or nickel to a temperature above 500°, germanium monoxide yields germanium dioxide and metallic germanium, the latter forming an alloy with the metal of the boat. When heated in boats of siliceous material the monoxide reacts above 800° to form yellow glazes.

Germanium monoxide is rapidly attacked by hydrogen chloride at about 175° with the formation of germanium chloroform and water. Chlorine attacks the oxide at 250°, forming $GeCl_4$ and GeO_2. No evidence of the formation of the oxychloride $GeOCl_2$, was obtained. The action of bromine is similar to that of chlorine.

Germanium Monosulfide

Germanium monosulfide was first described by Winkler,[2] and a study of its preparation by reduction of GeS_2 in hydrogen was made by Dennis and Joseph.[6] To obtain further information concerning the formation of GeS by precipitation of a solution of a germanous compound, and the properties of the resulting product, the present investigation was undertaken.

Experimental

Preparation of Germanium Monosulfide.—A solution of germanous chloride was prepared in the manner described under Germanium Monoxide. Hydrogen sulfide was passed into the hot solution and continued until the solution had cooled to room temperature. The precipitate under these conditions is dark red in color and granular. Precipitated from cold solution, the sulfide is light yellow and gelatinous. The red precipitate can readily be filtered and washed, and is quite stable toward oxygen at room temperature. Upon heating it to about 300° in pure nitrogen, all water was removed.

Analysis.—Germanium was determined by dissolving a sample in dilute ammonium hydroxide and 3% hydrogen peroxide that had been redistilled to free it from residue, evaporating the solution to dryness and carefully igniting the resultant GeO_2.

Sulfur was determined by the method of Popoff and Newman.[7]

Anal. Subs., 0.0970, 0.1340. Calcd. for GeS: Ge, 0.0673, 0.0930 = 69.37%. Found: Ge, 0.0671 = 69.22%; 0.0929 = 69.30%. Subs., 0.2236, 0.2571. Calcd. for GeS: S, 0.0685, 0.0788 = 30.63%. Found: S, 0.0684 = 30.59%; 0.0786 = 30.56%.

Properties.—Germanium monosulfide, thus prepared, is a dark red, amorphous substance; specific gravity, d_4^{20} 3.31. It is readily soluble in dilute hydrochloric acid, but is only slowly attacked by sulfuric, phosphoric or organic acids. It is rapidly oxidized by hot dilute nitric acid, and by aqueous solutions of hydrogen peroxide, potassium permanganate, chlorine or bromine.

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[6] Dennis and Joseph, *J. Phys. Chem.*, *31*, 1716 (1927).

[7] Popoff and Newman, *Ind. Eng. Chem., Anal. Ed.*, **2**, 45 (1930).

The red sulfide is readily soluble in solutions of alkali hydroxides or sulfides, forming deep red solutions, from which the addition of alcohol causes the separation of red, viscous liquids. The sulfide is slowly oxidized in air at 350°, and rapidly at higher temperatures, forming GeO_2 and SO_2. When heated to about 150° in hydrogen chloride, germanium chloroform and hydrogen sulfide are formed. Chlorine attacks the sulfide at room temperature forming $GeCl_4$ and chlorides of sulfur.

Crystalline Germanium Monosulfide.—When red, amorphous germanium monosulfide is held at 450° in an atmosphere of nitrogen, it changes in a few hours to the black crystalline form described by Dennis and Joseph.[6] The substance is slowly oxidized by an ammoniacal solution of hydrogen peroxide and also by chlorine water or potassium permanganate. It begins to sublime in nitrogen at 430°, and melts at 625°. Its specific gravity is d_4^{20} 3.78.

Summary

This article describes the preparation and properties of hydrous and anhydrous germanium monoxide, and of amorphous and crystalline germanium monosulfide.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

THE EFFECTS OF SUBSTITUENTS ON QUANTUM EFFICIENCY IN THE QUINONE-ALCOHOL REACTION

BY PHILIP A. LEIGHTON AND WILLIAM F. DRESIA

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The average of over twenty determinations[1] of quantum efficiency for the photochemical reaction between benzoquinone and ethyl alcohol in the wave length region λ4350–2537 Å. yields the figure 0.502. In other words, for every quinone molecule decomposed, two quanta are absorbed. The nearness of this ratio to one-half immediately raises interest as to its source.

Weigert and Brodmann[2] explained a quantum efficiency of one-half in the nitrobenzaldehyde photolysis as due to the different possible orientations of the absorbing molecules with respect to the electric vector of the incident light, by which statistically only one-half of the absorbed light could be effective in producing activation and subsequent chemical change.

By assuming a superoxide structure for quinone, the same explanation can be applied to the observed quantum efficiency in the quinone reaction. However, as was pointed out, the results can also be explained by assuming that every absorbed quantum is effective in producing activation, and that a 50% efficient secondary reaction is responsible for the observed yields.

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[1] Leighton and Forbes, THIS JOURNAL, 51, 3549 (1929).

[2] Weigert and Brodmann, *Trans. Faraday Soc.*, 21, 453 (1925).

Changes in quinone concentration throw no light on this question, the alcohol being present in such excess that the reaction is pseudomonomolecular, and the quantum efficiency hence independent of concentration within measurable limits. Very low concentrations of alcohol and quinone in a neutral solvent might be used to gain evidence on this point, but a simpler method offers itself in the possibility of substituting heavy groups in the quinone molecule. If the quantum efficiency of one-half is inherent in the process of absorption and activation of molecules of the nitrobenzaldehyde and quinone type, substituents should not affect it; but if a secondary reaction, involving collisions with a low probability of effectiveness, is responsible, substituents should offer a steric hindrance to the reaction, with a resultant change in quantum yield.

We have investigated, therefore, the effects of substitution in a series of chloro and aliphatic substituted quinones.

Apparatus and Materials

The monochromator described earlier was used,' with the addition between the front slit and the collimating lens of a quartz–water cell to cut down infra-red radiation. In this cell could be placed Corning glass filter combinations, which were used to increase the purity of those mercury arc lines lying in the visible region. For example, the separation of λ5460 from λ5770, imperfect with the monochromator alone or with filters alone, is almost complete with the combination of monochromator and filters.

The experimental procedure and method of calculation employed were the same as described.' Some trouble was experienced with the analysis in the case of the alkyl substituted quinones, but this was overcome by using more concentrated hydrogen iodide solutions and by titrating dark and exposed samples simultaneously.

Monochloroquinone was prepared by the oxidation of monochlorohydroquinone with dichromic acid.[3]

Dichloroquinone was prepared by the oxidation of symmetrical trichlorophenol with chromic acid.[4]

Toluquinone was prepared by oxidizing o-toluidine with manganese dioxide under steam distillation.[5]

Chloranil and thymoquinone were obtained commercially. All the quinones were carefully purified by successive sublimation before use.

Experimental

Measurements of the amount of quinone disappearing during the exposure and of the number of ergs of monochromatic energy absorbed by the quinone itself were used in calculating quantum efficiencies. All experi-

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[3] Den Hollander, *Rec. trav. chim.*, *39*, *481* (1920); Clark, *Am. Chem. J.*, 14, 571 (1892).

[4] Kehrmann and Tiesler, *J. prakt. Chem.*, [2] 40, 481 (1889).

[5] Clark, *Am. Chem. J.*, 14, 565 (1892).

ments were performed at 25°. Solutions were 0.005 *M* in absolute alcohol except that for chloranil an 0.0025 M solution was used. The solutions were kept under pure nitrogen at all times.

Alcoholic quinone solutions, especially those of the chloro-substituted quinones, decompose slowly in the dark, the average amount of decomposition being shown in Table I.

TABLE I

DARK REACTION (25°)

	Time, sec.	% Decomposed	Time. sec.	% Decomposed
Monochloroquinone	5660	1.0	10036	2.0
			15310	3.0
Dichloroquinone	4992	1.5	1926	1.0
Chloranil	6105	2.5		

The rate of the dark reaction apparently increases with amount of chlorine substitution.

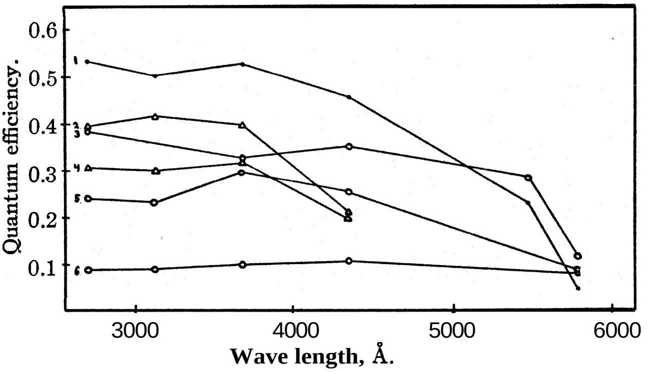

Fig. 1.—Relation between quantum efficiency and wave length. Circles represent chloroquinones; triangles, alkylquinones. 1, Benzoquinone; 2, toluquinone; 3, monochloroquinone; 4, thymoquinone; 5, dichloroquinone; 6, tetrachloroquinone.

Error from the dark reaction was avoided by always pipetting equal portions of solution into two similar cells, one being kept in the dark while the other was exposed, and both being analyzed simultaneously. Light reaction was then taken as the difference between dark reaction and total reaction.

In Table II, Q_m represents the fraction of the total incident energy of the entire exposure which was absorbed by the quinone alone,' and Φ represents the quantum efficiency, molecules/quanta. The individual values of Φ possess, in general, a probable error of ±10 to 15%.

Discussion

The quantum efficiencies are summarized in Table III, and compared on Graph 1.

Three points are to be observed. (1) For each quinone there is a region in which the efficiency of the reaction is, within limits of error, independent of the wave length. At longer wave lengths, however, for every quinone except chloranil there is a region in which the efficiency drops off rapidly. In other words, every quinone shows a threshold region below which the quantum efficiency is independent of wave length.

(2) This threshold region varies from one quinone to another—moving toward longer wave lengths with increasing chlorine substitution and toward shorter wave lengths with alkyl substitution. The oxidation potentials of the quinones are shifted in a similar manner, as shown by the following comparison.

Quinone	Oxidation potentials	Approximate threshold region, Å
Thymoquinone	0.5875	λ4000–4350
Toluquinone	.6454	40004350
Benzoquinone	.6990	4350–5000
Monochloroquinone	.7125	*circa* 5000
Dichloroquinone	,7220	*circa* 5000
Tetrachloroquinone	...	5770

TABLE II

λ	% Reduced	Q_m	Quanta absorbed	Molecules reduced	Φ
(a) MONOCHLOROQUINONE, $C_6H_3ClO_2$					
5770	3.70	0.016	4.88×10^{18}	5.61×10^{17}	0.115
5460	0.90	.042	4.80×10^{17}	1.36×10^{17}	.284
4350	6.6	.168	3.05×10^{18}	1.07×10^{18}	.350
3660	14.4	.564	7.03×10^{18}	2.33×10^{18}	.326
2700	13.8	1.0	5.80×10^{18}	2.27×10^{18}	.385
(b) DICHLOROQUINONE, $C_6H_2Cl_2O_2$					
5770	2 0	0 060	$3\ 54 \times 10^{18}$	$3\ 03 \times 10^{17}$	0.086
4350	14.2	.611	$5\ 74 \times 10^{18}$	$1\ 45 \times 10^{18}$	.253
3660	10 5	.729	$5\ 35 \times 10^{18}$	$1\ 59 \times 10^{18}$	.297
3130	13 5	.783	$9\ 24 \times 10^{18}$	$2\ 19 \times 10^{18}$	.234
2700	19 3	.905	$6\ 07 \times 10^{18}$	1.46×10^{18}	.241
(c) CHLORANIL, $C_6Cl_4O_2$					
5770	9.7	0.050	8.94×10^{18}	7.35×10^{17}	0.082
4350	3.6	.488	2.54×10^{18}	2.72×10^{17}	.106
3660	8.8	.676	7.22×10^{18}	7.13×10^{17}	.098
3130	5.4	.831	4.61×10^{18}	4.09×10^{17}	.089
2700	8.0	1.0	7.36×10^{18}	6.48×10^{17}	.088
(d) TOLUQUINONE, $C_6H_3(CH_3)O_2$					
4350	12.4	0.550	1.26×10^{19}	2.64×10^{18}	0.210
3660	14.4	.650	5.51×10^{18}	2.18×10^{18}	.396
3130	28.3	.870	1.03×10^{19}	4.29×10^{18}	.417
2700	20.6	.872	7.92×10^{18}	3.13×10^{18}	.395

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[6] La Mer and Baker, THIS JOURNAL, 44, 1960 (1922); Conant and Fieser, *ibid.*, 45,2208 (1923).

TABLE II *(Concluded)*

(e) THYMOQUINONE, $C_6H_2(CH_3)(C_3H_7)O_2$

λ	% Reduced	Qm	Quanta absorbed	Molecules reduced	Φ
4350	19.0	0.680	1.45×10^{19}	2.88×10^{18}	0.198
3660	21.8	.742	1.03×10^{19}	3.30×10^{18}	.320
3130	21.2	.915	1.08×10^{19}	3.21×10^{18}	.300
2700	15.8	.90	7.81×10^{18}	2.39×10^{18}	.307

TABLE III

SUMMARY OF QUANTUM EFFICIENCIES

Quinone	Mol. wt.	Φ at following wave lengths 5770	5460	4350	3660	3130	2700	Mean of quantum efficiency in constant region
Benzo	108	0.045	0.230	0.457	0.527	0.502	0.536	0.505
Tolu	122	..	..	.210	.396	.417	.395	.403
Monochloro	142.5	.115	.284	.350	.326	..	.385	.354
Thymo	164	..	..	.198	.320	.300	.307	.309
Dichloro	177	.086	..	.253	.297	.234	.241	.256
Tetrachloro	246	.082	..	.106	.098	.089	.088	.095

The oxidation potential indicates an increase in the activity of the quinones as one goes from thymoquinone to the chloroquinones. The threshold region, in shifting toward longer wave lengths, indicates for the same progression a decrease in the amount of energy needed to activate the molecule. The two effects are entirely in accord—the more active quinones require less energy for activation.

(3) The value of the quantum efficiency below the threshold (in the region where it is independent of wave length) also varies from one quinone to another. Here, however, the effect appears to be independent of the chemical nature of the substituting groups. *It is a function only of their mass.* This is brought out by comparing the mean quantum efficiency in the constant region with the molecular weight of the quinone (graph 2).[7]

We believe this to be purely a space effect. The effect on the threshold region shows that substitution influences the energy needed to activate the molecule. Once activated, its fate is determined by the probability of a reaction-producing collision with an alcohol molecule. This may be represented by the reaction scheme

$$\text{Quinone} + h\nu \longrightarrow \text{Quinone}' \qquad (1)$$

$$\text{Quinone}' \longrightarrow \text{Quinone} + \text{energy} \qquad (2)$$

$$\text{Quinone}' + \text{alcohol} \longrightarrow \text{Hydroquinone} + \text{aldehyde} \qquad (3)$$

The quantum efficiency then is determined by the relative probabilities of Reactions 2 and 3. The larger and heavier the molecule, the smaller the probability of a suitable collision, or, the smaller the relative proba-

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[7] It is to be noted that the alkyl quinones both deviate from the curve connecting the chloroquinones and benzoquinone. As this deviation lies just on the limits of experimental error, we cannot say that it is real.

bility of Reaction **3** compared with Reaction 2. The chemical nature of the substituting groups is without effect.

On this basis, the nearness of the quantum efficiency to one-half for benzoquinone can only be regarded as fortuitous, and the mechanism proposed by Weigert does not apply. Weight is added to this conclusion by the observation that in acid solutions the reaction rate is increased as much as 20%.

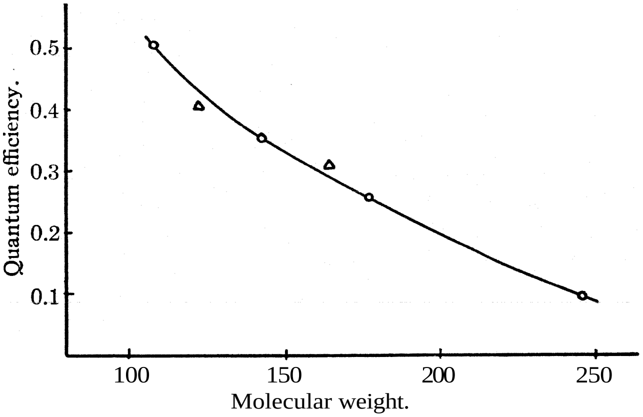

Fig. 2.—Showing relationship between quantum efficiency and the molecular weight of the quinone used. Circles are for chloro-substituted, triangles for alkyl-substituted, quinones.

Further measurements are in progress to determine whether the effects described here apply to other photochemical reactions. If found to be general, we believe these effects will give a valuable insight into the phenomenon of "steric hindrance" in chemical reactions. By the photochemical method of study it might be possible to separate pure space effects from those specific effects arising from the chemical nature of the substituents.

Summary

1. The quantum efficiencies of the photochemical decomposition of five chloro and alkyl substituted quinones in alcoholic solutions have been measured between A2700 and A5770 Å.

2. For each quinone, a threshold region, below which the efficiency is independent of the wave length, is observed.

3. Substituents which increase the oxidation potential of the quinone shift the threshold toward longer wave lengths and *vice versa.*

4. Substitution decreases the quantum efficiency as the mass of the molecule is increased, irrespective of the chemical nature of the substituents.

5. The specific effects on the threshold and the general effects on the efficiency are sharply differentiated. The first is ascribed to changes

produced by substitution on the energy of activation of quinone. The second is ascribed to a "steric hindrance" affecting the probability of reaction of the activated molecule.

STANFORD UNIVERSITY, CALIFORNIA

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

THE SENSITIZED PHOTOSYNTHESIS OF CARBON DIOXIDE AT LOW CHLORINE PRESSURES

BY G. K. ROLLEFSON

RECEIVED JUNE 10, 1930 PUBLISHED SEPTEMBER 5, 1930

In studying the photosynthesis of phosgene, Chapman and Gee[1] found that oxygen had an inhibiting effect on the reaction. Later Bodenstein[2] showed that the concentration of the oxygen did not remain constant during the reaction, but decreased, due to the formation of carbon dioxide. Schumacher,[3] in a more extensive investigation, found that at high oxygen pressures the phosgene formation was so small that it could be neglected for chlorine pressures below 50 mm. In this case the oxygen and carbon monoxide reacted to form carbon dioxide, the rate law being

$$\frac{d(CO_2)}{dt} = kI_{\text{abs.}}^{0.71}\,(CO)^{1/2}$$

or for small absorption of light

$$\frac{d(CO_2)}{dt} = kI_0^{0.71}\,(Cl_2)^{0.71}\,(CO)^{1/2}$$

where I_0 is the intensity of the incident light. The exponent, 0.71, for the light absorbed suggests at once that the conditions were probably such that two parallel reactions were involved, one being proportional to the first power of the light absorbed, the other to the square root. A case of this type was shown to exist in the photosynthesis of hydrobromic acid.[4,5] That reaction followed the square root law at high pressures and the first power at low pressures. It seemed not unreasonable to think that in the sensitized formation of carbon dioxide a similar behavior should be found so that at high pressures of chlorine the square root of the light absorbed would appear in the rate law and at low pressures the first power. In both reactions the explanation of this behavior would be the same, *i. e.*, the destruction of the halogen atoms by first order reactions such as collisions with the walls of the reaction vessel or with impurities predominates at low pressures, whereas the recombination in the gas phase is of greater importance at high pressures.

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[1] Chapman and Gee, J. *Chem. Soc.*, 99, 1726 (1911).

[2] Bodenstein, *Sitzb. preuss.* Akad. *Wiss.*, 13, 104 (1926).

[3] Schumacher, *Z.* physik. *Chem.*, 129, 241 (1927).

[4] Briers and Chapman, J. *Chem. Soc.*, 130, 1802 (1928).

[5] Jost and Jung, Z. physik. *Chem.*, B3, 83 (1929).

Experimental

From Schumacher's results it seemed that the first power law must hold at pressures of chlorine below two centimeters of mercury; therefore the apparatus used in these experiments was designed for work in that range. The reaction vessel was made of pyrex, cylindrical in form with a plane window at one end and the inlet for the gases at the other. The length of the vessel was 18 cm. and the diameter 6 cm. Uniform illumination was obtained by rendering the light from a 500-watt tungsten filament lamp approximately parallel and passing it through a solution of quinine sulfate to remove rays of wave length less than 4050 Å. It is readily shown that under such conditions the change in intensity of the effective light in passing through the reaction vessel is never more than 10% if the pressure of chlorine is less than 2 cm. of mercury. Furthermore, the deviation from strict proportionality between the amount of light absorbed and the chlorine pressure is less than 5%.

The chlorine was prepared by heating anhydrous cupric chloride in a small side tube sealed onto the tube leading into the reaction vessel. The gas prepared in this manner has been tested previously and found thoroughly satisfactory.[6] The carbon monoxide was prepared by the decomposition of formic acid in sulfuric acid, washed with strong sodium hydroxide solution and finally dried with concentrated sulfuric acid. The gas was stored in a three-liter bulb from which it could be admitted to the reaction vessel as needed. The oxygen was prepared by the electrolysis of potassium hydroxide solution, was freed from hydrogen by passing over hot copper oxide, and was stored in a three-liter bulb containing some anhydrous calcium chloride which served as a drying agent.

The reaction was followed by observing the change in pressure with time. Due to the marked heating which occurs during the reaction, all readings were taken after turning off the light and allowing the system to stand until the pressure became constant. The manometer liquid was sulfuric acid of specific gravity 1.84. As the total pressure used in these experiments was of the order of half an atmosphere, a special form of manometer had to be devised in order to keep the length of the column to be measured within reasonable dimensions. The form finally adopted consisted of a vertical section of glass tubing, internal diameter 3 mm., the upper end of which was connected to the reaction vessel by means of a capillary tube and the lower end was ring-sealed into a flask of one-liter capacity in such a manner that the end dipped into thirty cubic centimeters of sulfuric acid in the bottom of the flask. Another tube leading out of the flask permitted either the simultaneous evacuation of both sides of the manometer or the admission of air into the flask to any desired pressure. Thus the manometer read the difference in pressure between the reaction vessel and the other side. For any one setting the range was approximately 50 cm. of sulfuric acid or 6.75 cm. of mercury. Pressure changes beyond this range were read by resetting the manometer as many times as necessary.

The procedure followed in making a run was to introduce chlorine into the reaction vessel up to a pressure 8–10 cm. of sulfuric acid above that to be used in sensitizing the carbon dioxide formation. Next the carbon monoxide was admitted from the reservoir bulb. These two gases were illuminated with resultant phosgene formation until the chlorine pressure had been reduced to the value desired for the run. This procedure was considered necessary by Schumacher in order to destroy inhibitors which would otherwise cause an induction period in the carbon dioxide formation. Some preliminary tests with the materials used in these experiments showed that frequently this procedure was unnecessary in order to obtain results free from an induction period but the number of

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[6] Rollefson, THIS JOURNAL, 51, 770 (1929).

cases in which the induction period appeared was sufficient so that it was deemed expedient to carry out the reaction as recommended by Schumacher. After this preliminary formation of phosgene, the oxygen was admitted to a pressure 80–100 cm. of sulfuric acid in excess of the amount required for complete oxidaton of the carbon monoxide. A period of from one to three hours was allowed for the gases to mix before starting the reaction. In following the reaction readings were taken at intervals of from one-half to five minutes depending on the speed of the reaction.

Results

The data obtained are summarized in graphical form. Under the conditions of the experiments the amount of phosgene formed should be negligible and the rate independent of the oxygen pressure so that at a given chlorine pressure the observed law should be

$$-\frac{d(CO)}{dt} = k(CO)^{1/2}$$

Integrating this expression

$$(CO)^{1/2} = kt + a$$

where *a* is the constant of integration. Hence if we plot the square root of the carbon monoxide pressure against the time, the resulting curve should

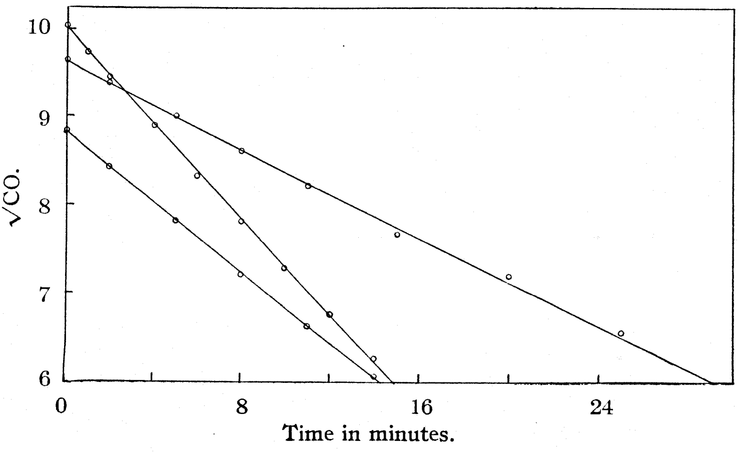

Fig. 1.

be a straight line. Pigure 1 shows the curves obtained at three different chlorine pressures. In each case the straightness of the line[7] shows that the assumptions of constancy of the chlorine pressure during the run and independence of the rate from the oxygen pressure are valid.

The effect on the rate of varying the chlorine pressure is obtained by plotting the values of k obtained above against the chlorine pressure raised to such a power that a straight line is obtained. Figure 2 shows the plot using the first power of the chlorine pressure and it is obvious that this law holds well within the limits of error of the experiments.

[7] In these plots the pressures have been left in terms of cm. of sulfuric acid.

It remains to show the effect of varying the intensity of the incident light. The procedure followed was to illuminate a given reaction mixture for three-minute intervals, using various screens to reduce the light intensity. The screens were of black cloth and had been calibrated with a thermopile and tested for neutrality. In Fig. 3 the observed rates are plotted against the light intensity, the intensity with no screen being taken as one. The circles were obtained with one reaction mixture and the crosses with another. The point on the abscissa axis represents the amount of reaction produced by light reflected from the walls of the room and surrounding objects. Another source of error which would be of consequence at low light intensities, but could not be corrected for, is the variation in light intensity due to imperfections in the filters. The graph shows that the rate of reaction is proportional to the first power of the light intensity.

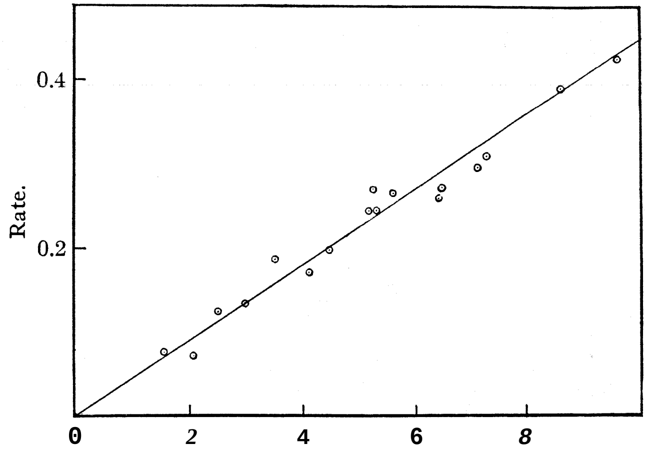

Fig. 2.

Discussion

From the data which have been presented, we see that at low pressures of chlorine the rate of formation of carbon dioxide is given by the expression

$$\frac{d(CO_2)}{dt} = kI_{abs.}(CO)^{1/2} = kI_0(Cl_2)(CO)^{1/2}$$

where the substitution of $I_0(Cl_2)$ for $I_{abs.}$ is justified by the fact that the total amount of light absorbed is small. This result confirms the view expressed at the beginning of this paper, to the effect that the exponent 0.71, found by Schumacher, is due to a mixture of reactions. The extension of the measurements to cover the pressure range studied by Schumacher has been delayed pending the construction of an apparatus which will permit the simultaneous observation of the carbon dioxide formation and the phosgene formation which is always present at high chlorine pressures. It may be that the deviation from the first power of the chlorine pressure at high pressures is due to the formation of phosgene, causing a break in the chain of reactions giving carbon dioxide, which would result in the observed yield being less than it would be if the phosgene formation remained negligible. This possibility is to be investigated.

Turning to a consideration of the possible mechanisms for the carbon dioxide formation, we find that the equations given by Bodenstein, Lenher and Wagner[8] and by Lenher and Rollefson[9] agree in that both have the carbon dioxide formed by the action of oxygen on an intermediate compound $COCl$. No detailed calculations concerning the formation of carbon dioxide were made in either paper as both were primarily concerned with the formation of phosgene. Some attempts have been made to calculate the rate law obtained in this paper from those mechanisms, but they have been unsuccessful, as the derived equations either showed a dependence of the rate on the oxygen pressure, or else gave the wrong exponents for the factors involved. These difficulties may be due to using the wrong chain-terminating reaction, although several different ones were tried. It is, however, possible to draw some conclusions concerning the nature of the

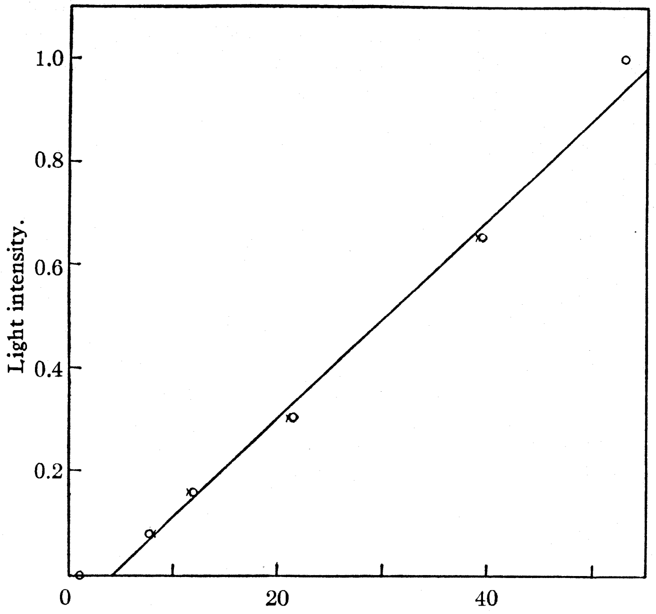

Fig. 3.

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[8] Bodenstein, Lenher and Wagner, *Z. physik. Chem.*, B3, 459 (1929).

[9] Lenher and Rollefson, THIS JOURNAL, 52, 500 (1930).

reaction. In the first place the fact that the rate of the reaction is independent of the oxygen pressure at moderate pressures of oxygen, but not at lower pressures, indicates that in the higher range the step involving oxygen is too fast to be one of the rate-determining steps; therefore, on the basis of both the mechanisms referred to above, the rate of formation of carbon dioxide is essentially the rate of formation of COCl. Now it is an experimental fact that the rate of oxidation of carbon monoxide at a given chlorine pressure is comparable with the rate of formation of phosgene, at the same chlorine pressure, in the absence of oxygen. On the basis of the mechanism of Bodenstein, Lenher and Wagner, this would mean that their Reactions 2 and 4, namely

$$CO + Cl = COCl, \text{ and}$$
$$CO + Cl_2 + Cl = COCl_2 + Cl$$

have comparable rates. Such being the case, it is difficult to see how it would be possible for the phosgene formation to be negligible at any moderate pressure, as is found to be the case. This difficulty does not exist in the mechanism of Lenher and Rollefson, as COCl is a step in the formation of phosgene in that mechanism so that if the COCl is removed rapidly by oxygen, the rate of formation of phosgene will drop to a low value. At high temperatures the rate of dissociation of COCl becomes faster than the rate of reaction with oxygen, and therefore the carbon dioxide formation ceases at such temperatures. From this viewpoint the sensitized photosynthesis of carbon dioxide supports the views of Lenher and Rollefson concerning the formation of phosgene. Further discussion of this system will be postponed until more data are available.

Summary

The chlorine-sensitized photosynthesis of carbon dioxide has been studied for pressures of chlorine ranging from 2 to 13 mm. of mercury. In this range the rate law has been shown to be

$$\frac{d(CO_2)}{dt} = kI_0(Cl_2)(CO)^{1/2}$$

The results have been discussed briefly from the standpoint of the mechanisms which have been proposed by Bodenstein, Lenher and Wagner, and by Lenher and Rollefson.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE USE OF CALCIUM HYDRIDE FOR THE DETERMINATION OF THE SOLUBILITY OF WATER IN BENZENE, CARBON TETRACHLORIDE AND TOLUENE

BY CHESTER K. ROSENBAUM[1] AND JAMES H. WALTON

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Introduction

For the determination of small amounts of water, 0.1% or less, a gasometric method has the advantage of giving a relatively large volume of gas from a small amount of water. Various reagents have been used to react with water to evolve a gas the volume of which was measured. Calcium carbide was used by Roberts and Frazer[2] and other investigators. Sodium[3] and the Grignard reagent[4] have also been used.

The energetic reaction of calcium hydride with water to evolve hydrogen suggested its use for the determination of water. The hydride offers two advantages over calcium carbide: (1) in most reagents the hydrogen evolved is not as soluble as acetylene and (2) the experimental accuracy is greater since, according to the following equations, twice the volume of gas is evolved:

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$$
$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

Calcium hydride has been used by Wirth[6] to determine water in ethyl alcohol using the reaction

$$CaH_2 + CO_2 + H_2O = CaCO_3 + 2H_2$$

His results, however, are of doubtful value because of the possible reaction of calcium hydride with the alcohol to evolve hydrogen.[6]

Since the completion of the work reported in this paper, an article has been published describing a method developed by Olav Notevarp,[7] who used calcium hydride to determine the water content of various solids and high-boiling liquids. The two methods, developed simultaneously and independently, are radically different since in Notevarp's method the hydride is suspended above the sample and does not mix with it. He found his apparatus to be impractical for determinations of water in low-boiling

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[1] Part 2 of a dissertation submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Roberts and Frazer, J. *Soc. Chem. Ind.*, 29, 197 (1910).

[3] Graefe, *ibid.*, 25, 1035 (1906).

[4] Zerewitinoff, *Z. anal. Chem.*, 50, *680* (1911).

[5] Wirth, *Z. Deut. dl-Fett-Ind.*, *41,* 147 (1921).

[6] Moissan, *Compt. rend.*, 127, 29 (1898); B. von Lengyl, *Math. Nat. Ber. Ungarn.*, 14, 180 (1898); Perkin and Pratt, J. *Chem. Soc.*, 95,161 (1909).

[7] Olav Notevarp, *Z. anal. Chem.*, 80, 21 (1930).

organic solvents such as were used in the present investigation. Also, his analyses were concerned with various practical determinations in which larger percentages of water were present.

The present investigation was begun by studying the determination of water in benzene since the latter does not react[8] with the calcium hydride. The method developed was then extended to other solvents.

Experimental

Materials

The benzene was reagent grade, found free from thiophene, and had a boiling point 79.6° (corr.) and melting point 5.4° (corr.).

The carbon tetrachloride was found to be free from all impurities (boiling point 76.8° corr.).

The toluene was purified by standing over mercury, refluxing with phosphorus pentoxide and fractionating, the fraction distilling at 110.4–110.6° being used.

The calcium hydride was found to be about 97% pure. The chief impurity was about 2% calcium nitride as determined by acid titration of the ammonia evolved in the reaction with water. It contained about 0.2% of calcium carbide and possibly some metallic calcium and calcium oxide. None of these impurities interfered with the determinations, as will be shown later by the results in Table I.

Apparatus.—In the type of apparatus used by McNeil,[9] calcium carbide was dropped from a side arm into the sample contained in a flask connected with a gas buret. This gave inaccurate results when calcium hydride was used to determine water in benzene. The errors introduced by such an apparatus are as follows. (1) The largest error is due to adsorbed gases found present on the powdered calcium hydride. A considerable volume of gas was released when the hydride was heated in a tube or when the powder was dropped into a dry organic liquid. (2) A film of moisture remains on the reaction flask despite drying at 110° and is also adsorbed during the manipulations. (3) Any rubber present is attacked by the organic vapor with consequent leaks and introduction of impurities.

These errors are eliminated in the apparatus shown in Fig. 1, which is constructed as follows: a 150-cc. pyrex flask A is connected by the ground-glass stopcock B with the 50-cc. bulb C fitted with a ground-glass joint D. The ground-glass joint F is tightly held together by the rubber bands G stretched between wires encircling each half of the joint. The tube J is partly filled with calcium hydride to insure reaction of any water in the organic vapor with the hydride before it reaches the phosphorus pentoxide placed in the tube K. The rubber connection L is surrounded by a well of mercury M to prevent gas leakage. The 100-cc. gas buret N and the leveling tube P are filled with water. Constant temperature is maintained by pumping water at 30° from a thermostat through H, O, and the bath Q.

Method.—The apparatus was prepared for an actual water determination by the following preliminary treatment. About 5 g. of powdered calcium hydride was placed

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[8] Moissan, *Compt. rend.*, 127, 29 (1898); Reich and Serpek, *Helv. Chim. Acta.*, **3, 138 (1920).**

[9] McNeil, U. S. Dept. Agr., Bur. *Chem. Circ.* 97, pp. 1–8.

in the flask A with about 15 cc. of the undried solvent being studied. The ground-glass joints were then lubricated by a special graphite paste made by mixing dry graphite powder (100 mesh) with just enough stopcock grease to give a thick paste. This special preparation was found necessary because the hot organic vapors dissolved the ordinary lubricants with consequent leakage. The flask **A** was then put in place as shown in Fig. 1 and was heated for several hours. This heating was conveniently accomplished by a small electric heating coil. After several hours the heating coil was removed from beneath A, the flask was allowed to cool and the thermostat Q was raised into place around A. After the system had come to equilibrium the gas volume was read. The barometric pressure was also recorded, since it was found that 1 mm. change in atmospheric pressure resulted in a change of 0.3 to 0.5 cc. in the gas volume (depending on the volume of gas present in the apparatus); this correction was always applied when any change in pressure occurred. The thermostat Q was then lowered and the heating of the flask continued for several hours. The heating coil was then removed from beneath **A,** Q was raised into place and a reading taken of gas volume and barometric pressure. The process of heating, cooling and taking readings was continued until no more hydrogen was evolved. This preliminary treatment served a three-fold purpose: (1) it checked the apparatus for leaks, (2) it removed any moisture in the apparatus, (3) it removed the adsorbed gases from the calcium hydride.

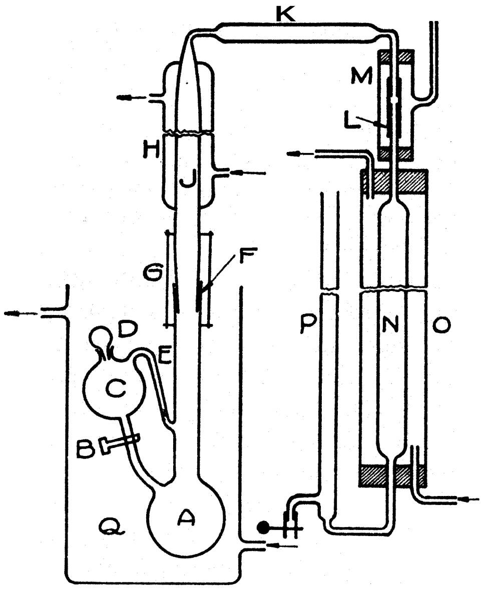

Fig. 1.—Apparatus for water determination.

After the above procedure the actual determination of water was carried out as follows. The organic solvent was first saturated by shaking with water in a flask at high temperature and then allowing the flask to cool in a thermostat to the desired temperature, with the resulting separation of excess water as shown by the turbidity. The solution was allowed to stand for a day or more to come to equilibrium before a sample was withdrawn for solubility measurements. The sample was then withdrawn with a 25-cc. pipet, the tip of which was guarded by a ground-glass cap and the upper end by a tube filled with calcium hydride to prevent absorption of moisture when not in use. The sample (**25** or 50 cc.) was introduced into the bulb C through D after B had been closed. The joint D was then closed and the bath Q raised around A. After the system had come to equilibrium, the initial gas reading and barometric pressure were recorded. The bath Q was then lowered and B was opened to allow the sample to react with the calcium hydride already present with the dry solvent in A. Hydrogen was evolved rapidly at first and after the evolution slowed down, the flask was heated to expedite the reaction. The process of heating, cooling and taking readings was continued until it was found that no more gas was being evolved. In some cases the reactions were allowed to continue for three days before the last traces of gas were evolved, although it was found that the reaction was about **95%** complete within the first ten hours.

After one determination was completed, another sample was added to the flask and successive analyses were carried out until the flask A was filled with the solvent.

Results.—The accuracy of the method was first established by adding a weighed amount of water from a weighing pipet to calcium hydride contained in benzene from which all water had been abstracted by boiling with the hydride until no more hydrogen was evolved. The results of these experiments are shown in Table I.

TABLE I

ACCURACY OF METHOD

Experiment	1	2	3
Water taken, g.	0.0387	0.0396	0.0406
Hydrogen evolved (calcd. as water), g.	.0384	.0396	.0402

Solubility of Water in Benzene, Carbon Tetrachloride and Toluene.—The solubility of water in the above solvents was determined at various temperatures. The results are shown in Table II and are graphed in Fig. 2.

TABLE II

SOLUBILITY OF WATER IN BENZENE, CARBON TETRACHLORIDE AND TOLUENE

Temp., °C.	Grams of water per 100 g. of solvent Benzene	Carbon tetrachloride	Toluene
10	0.0451	0.00711	0.0335
20	,0573	.00844	.0450
30	.0746	.0109	.0600
40	.0953	.0152	.0733
50	.1271	.0237	.0953
60	.1637	....	....

(a) Solubility of Water in Benzene.—The values given in the table are an average of two to four determinations of the solubility at each temperature. A typical example of the accuracy of the individual determinations is illustrated by values of 0.0962, 0.0953 and 0.0944 (average 0.0953) for the solubility of water in benzene at 40°.

These results for the solubility of water in benzene are higher than those obtained by Clifford[10] by absorbing the moisture from the benzene with calcium chloride. They are somewhat lower than the results of Groschuff[11] determined by the turbidity method and also lower than the results of Hill[12] determined by measuring the solubility of silver perchlorate in benzene–water solutions.

As a practical application of this method of analysis, the drying of benzene by distilling off and discarding the first 10% was tested. This method is recommended for the removal of water from benzene.[13] Ordinary tech-

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[10] Clifford, *Ind. Eng. Chem.*, 13,632 (1921).

[11] Groschuff, Z. *Elektrochem.*, 17,348 (1911).

[12] Hill, THIS JOURNAL, 45, 1143 (1923).

[13] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1924, Vol. IV, p. 81.

nical benzene was used and in Table III the effect of distilling off 10% of Sample No. 1 was determined. Sample No. 2 was first saturated with water and 20% of the solution was distilled before the distillate came over unclouded, thus showing no more excess water.

TABLE III

THE REMOVAL OF WATER FROM BENZENE BY DISTILLATION

Sample No. 1. 10% distilled	Sample No. 2. 20% distilled
Original sample 0.025% H_2O	**Original sample 0.0746% H_2O**
Residue contained 0.0147% H_2O	**Residue contained 0.0156% H_2O**

(b) Solubility of Water in Carbon Tetrachloride.—The results given in Table II were obtained using 50-cc. samples and despite the very low solubility the method gave checks between individual determinations of 0.0004% H_2O. Clifford[10] using the calcium chloride method obtained values of 0.010% at 24° and 0.013% at 28.5°, the latter not agreeing with the present results.

The presence of carbon disulfide as an impurity in technical carbon tetrachloride was found to increase the solubility of water in the solvent by about 50%. As an example typical of several determinations, the solubility of water in carbon tetrachloride containing carbon disulfide was found to be 0.0170% instead of the value 0.0109% H_2O in pure carbon tetrachloride.

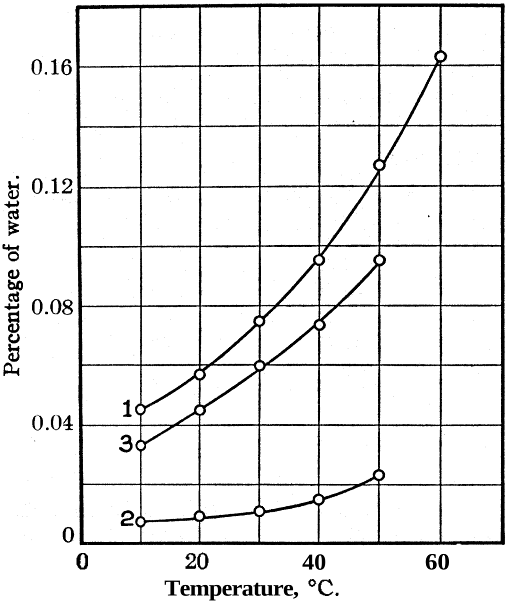

Fig. 2.—Solubility of water in organic solvents: Curve 1, benzene; Curve 2, carbon tetrachloride; Curve 3, toluene.

(c) Solubility of Water in Toluene.—The results given in Table II are average values obtained with 25- and 50-cc. samples of toluene.

Discussion

The principal value of the present method is its extreme accuracy. As shown by the results in Table I and the individual solubility determinations, the method is accurate to about 0.001% H_2O in determinations of less than 0.10% H_2O present in organic solvents.

A possible practical application of the method besides its use in solubility studies is as follows. A dry organic solvent such as benzene could be used to extract the water from a solid sample by leaching or refluxing and the water present in the solvent could subsequently be determined.

The two chief objections to the calcium hydride method are the following. First, the method is limited to solvents which do not react with calcium hydride or otherwise react so slowly that necessary corrections can be applied; second, the method is not rapid, since the analyses are of one to three days' duration, although they do not require much actual time or care. The time required can be shortened for practical determinations since the reaction is about 95% complete in ten hours and the percentage of total moisture could then be estimated.

Summary

1. A new improved apparatus and method have been developed for the gasometric determination of water in certain organic solvents.

2. Calcium hydride has been shown to be a good reagent for the quantitative determination of water, giving an accuracy of 0.001% H_2O in determinations of about 0.1% H_2O.

3. The solubility of water in benzene, in carbon tetrachloride, and in toluene has been determined at various temperatures.

4. Benzene can be dried to a water content of 0.015% by distilling and discarding the first 10 to 20% of the liquid.

MADISON, WISCONSIN

[CONTRIBUTION PROM THE DEPARTMENT OP CHEMISTRY, UNIVERSITY OF CINCINNATI]

A STUDY OF THE PRODUCTS OBTAINED BY THE REDUCING ACTION OF METALS UPON SALTS IN LIQUID AMMONIA SOLUTION. III. THE ACTION OF SODIUM UPON SILVER IODIDE AND SILVER CHLORIDE[1]

BY WAYLAND M. BURGESS AND EDWARD H. SMOKER

RECEIVED JUNE 18, 1930 PUBLISHED SEPTEMBER 5, 1930

Introduction

In the first paper of this series,[2] there was described a reaction in liquid ammonia between sodium and a salt, which resulted in the formation of a compound of sodium and the reduced metal. In the present paper a simpler case is presented where the reduced metal is obtained without further reaction.

Kraus and Kurtz[3] found that sodium reacted readily with silver cyanide

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[1] This article is based upon the thesis presented to the Faculty of the Graduate School, University of Cincinnati, by Edward H. Smoker in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Burgess and Rose, THIS JOURNAL, 51,2127 (1929).

[3] Kraus and Kurtz, *ibid.*, 47, 43 (1925).

or silver iodide in liquid ammonia, forming a metallic precipitate, inactive toward air and moisture. The reaction ratio of sodium to silver salt was given as 1.11 and 1.09. They concluded that no compound of sodium and silver was formed. A more accurate determination of this reaction ratio has been carried out, obtaining as an average value 1.00. The product of the reaction has been purified and shown by analysis to be metallic silver.

Experimental Method

Silver iodide (or silver chloride) was prepared by slowly mixing equal volumes of approximately 0.5 N solution of purified potassium iodide (or potassium chloride) and silver nitrate. The resulting precipitate was washed, filtered, dried at 110°, pulverized and kept in a brown bottle.

In carrying out the reaction, a small bent tube, containing a weighed amount of the silver salt, was placed in the side arm of a reaction tube, identical with the one used in the earlier work.[2] By gently tapping the tube, the powdered salt was slowly added to a liquid ammonia solution, containing a weighed amount of sodium, until the blue color just disappeared. The end-point of the reaction could be judged very accurately. From the weights of the silver salt and sodium used, the reaction ratio was calculated.

The precipitate formed by the reaction was washed according to the method previously described,[2] until the wash solution gave no test for soluble halides. The last trace of ammonia was allowed to evaporate against a slight pressure. Tests showed that the dried product did not gain weight in air, so it was removed from the reaction tube and weighed directly on a balance. The solid was then analyzed for silver by dissolving in concentrated nitric acid and precipitating as silver chloride. On a number of samples, determination of the loss in weight on heating to 100° and tests for iodides (or chlorides) and ammonia were made.

Experimental Data

In Tables I and II are summarized the experimental results for the reaction ratios and silver determinations.

TABLE I

REACTION RATIO AND SILVER ANALYSES USING SILVER IODIDE

No.	Na, g.	AgI, g.	Ratio Na/AgI	% Ag in product
178	0.1584	1.5981	1.012	96.4
179	.1581	1.5833	1.019	97.3
180	.1543	1 5728	1.000	97.1
194	.3181	3.2505	0.998	98.4
195	.2846	2.8812	1.008	98.3
198	,4652	4.7343	1.003	98.4

TABLE II

REACTION RATIO AND SILVER ANALYSES USING SILVER CHLORIDE

No.	Na, g.	AgCl, g.	Ratio Na/AgCl	% Ag in product
R3	0.4789	2.9957	0.997	..
B4	.4291	2.5840	1.007	98.8
B5	.4867	2 9451	1.030[a]	98.2
S1	.1756	1.0917	1.003	08.7
L1[b]	.2853	1.7751	1.002	..
L2	.2804	1.7458	1.001	..
L3	.2346	1.4644	0.999	..
L4	.2584	1.6118	.999	..

[a] Solution blue at end. [b] Those experiments marked I, carried out by Mr. Hooper Linford in this Laboratory.

Several samples showed a slight loss in weight on heating to 100° in an evacuated tube for several hours. The loss was of the magnitude of 0.1–0 . . In all cases, traces of iodides (or chlorides) were present in the product since the concentrated acid solution was always turbid. In a number of cases the dried precipitate was digested with water and the soluble iodides (or chlorides) determined. The values obtained varied from 0.1 to 0.8% of the total weight. Test made on the heated samples with Nessler's reagent showed that no ammonia was present. No gas was liberated during the reaction.

Discussion of Results

Both the reaction ratio and analysis of the product show that sodium reacts with silver iodide (or silver chloride) in liquid ammonia according to the following equation

$$Na + AgI \longrightarrow NaI + Ag$$

A product analyzing 100% silver could not be obtained because of the inability to wash the precipitate entirely free of adsorbed salts. That this was not due to inefficient washing was shown by digesting a dried sample with water before treatment with acid. Even then the acid solution was turbid, showing the presence of halogens.

The excellent agreement of the reaction ratio shows the high degree of accuracy with which the end-point of these reactions can be determined. It is suggested that free sodium in solution can be accurately determined by this method of adding a weighed quantity of silver chloride.

Summary

Sodium reacts with liquid ammonia solutions of silver iodide, or silver chloride, to form free silver and the corresponding sodium salt. No further reaction occurs.

CINCINNATI, OHIO

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

THE REMOVAL OF GASES FROM LIQUIDS

BY ROGER K. TAYLOR

RECEIVED JUNE 24, 1930 PUBLISHED SEPTEMBER 5, 1930

The complete removal of gases from liquids is essential in some research problems, and is a matter presenting considerable difficulty. Although the distribution coefficient of many gases between the vapor and liquid phases of the solvent is of such magnitude as to indicate that practically all of the gas should be removable by sweeping off a comparatively small amount of the solvent, the establishment of equilibrium is usually very slow; the rate of liberation of dissolved gas is dependent on the extent, and particularly on the rate of renewal, of the liquid–vapor interface. Periodic removal of the vapor above a liquid standing in a bulb is a very tedious method of accomplishing gas removal, since diffusion of the gas to the liquid–vapor interface is slow. Stirring the liquid, especially if it can be spread out in a large thin film, accelerates the process considerably. This can be accomplished in an apparatus previously described.[1]

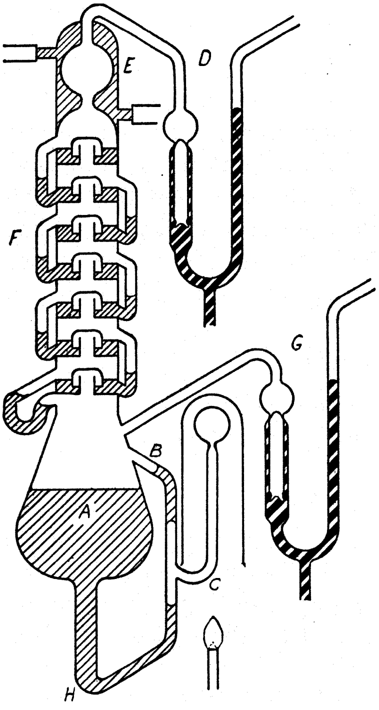

Fig. 1.

In another apparatus devised by the author, and shown in Fig. 1, the removal of air or other gas from any liquid of appreciable vapor pressure may be readily accomplished. The liquid is contained in **A**; most of the gas in the apparatus is pumped out through D. Then, with D closed, a small flame is placed under the side tube *C*, and cold water is circulated through the jacket E. The vaporization of the liquid in *C* carries a succession of slugs of the liquid up the tube B, splashing it against the opposite wall and permitting it to flow in a thin film down the wall, back to the bulk of the liquid. This action gives constant circulation and stirring of the liquid and active motion of the liquid–vapor interface.

C is sealed in somewhat above the center of B, so that even if B is for a moment completely filled with liquid, no opportunity is offered for vapor to push back to or past H. The liquid level in **A** must of course be somewhat above the junction of B and C. The constriction and bulb at the top of *C*, and jacket around *C*, are to keep this tube ever from filling completely with liquid, either by distillation or splashing; the heating of a nearly gas-free liquid at any considerable distance from a liquid–vapor interface leads to irregular, practically explosive, boiling and possibly disastrous bumping.

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[1] Taylor, THIS JOURNAL, 50,2937 **(1928).**

When sufficient condensation has taken place in E to give overflow from all of the sections of the column F, the latter functions like any fractionating column. The mixture of gas and vapor passes up the column, bubbling through the liquid on each plate, and the only way for gas to pass from any given section to the one below is to return in solution in the overflow. The partial pressure of gas (and hence its solubility) is low; the volume of condensate, compared with that of the vapor forming it, is very small. Accordingly a state of equilibrium will finally be reached at which virtually all of the gas in the system is in the top of the column, since the ascending vapor in each section will be relatively richer in gas than the descending liquid; the slowly descending liquid is stripped of its gas content by meeting in counter-current the ascending practically gas-free vapor. It is evident that when equilibrium as to gas content is reached, the liquid in A will be nearly gas-free even when the partial pressure of gas at the top of the column is quite appreciable. Incidentally, a rough estimate of the amount of gas present may be made by comparing temperatures at A and at the top of F; for obvious reasons the presence of gas will lead to a higher temperature at **A,** while when the gas is nearly all gone the slight difference due to the head of liquid through which the vapor must bubble is not appreciable to the touch.

The gas is removed as it accumulates, together with some of the vapor, by opening periodically the trap D for an instant to a pump or to an evacuated space of some five or ten times the volume from the top plate to the trap. Active bubbling up the column, persisting for some time, follows this operation if gas has accumulated to any extent.

Trap G communicates with the apparatus in which the gas-free liquid is to be used; at the proper time the receiver is chilled, and when G is opened the liquid distils over. Or, of course, the unit itself may be employed as a reservoir for the gas-free liquid.

The advantages of this over the apparatus previously described[1] are that with the same amount of stirring the gas–vapor mixture need not be removed so frequently; if equilibrium is established before each removal, the same number of removals carries off a far larger fraction of the gas; hence, though the loss of liquid in complete degassing is small in either case, it is less with the present device; and the slight chance of carrying air in mechanically with the flowing mercury of the former apparatus is obviated with this one. Furthermore, even if there should be a minute leak admitting air into the system, it would still be possible to withdraw a practically air-free vapor through G, as the air would be carried out of A up the column as it leaked in.

On the other hand, the present apparatus cannot be used as well as the former if it is necessary to maintain the liquid at a constant temperature during the degasification.

A device of the present sort has a number of uses. (1) At this University it has served for the preparation of air-free water, benzene and toluene, used in several researches.

(2) The author has employed it in a study of the retention in *vacuo* of gases by soluble salts. In this instance air-free water was admitted, by breaking a septum with a magnetically operated hammer, to an evacuated tube sealed on at H containing the salt under investigation; after the salt had dissolved, the solution was degassed as described above; the gas liber-

ated, together with some water vapor, was pumped off at D for measurement and analysis.

(3) It could evidently be used to determine the solubility of gases in liquids, by admitting the saturated liquid into the evacuated apparatus and pumping off and measuring the gas liberated.

(4) Adsorption of gases by soluble materials could be determined by a method similar to that used in (2).

A modified Töpler pump, embodying the features of the McLeod gage, has been found convenient in handling small amounts of gases, as in (2). Such an apparatus as shown in Fig. 2 may well be used in any case, such as (2), (3) and (4), when the amount and nature of the gas evolved are of interest.

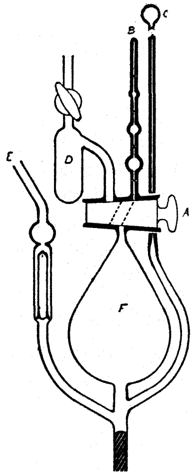

Fig. 2.

By raising the mercury, gas that has entered at E is compressed into the calibrated tube B up to one of the graduations, and the pressure is determined by comparing mercury levels in B and C. (Condensation of solvent vapor occurs in both B and C, so that vapor pressure is canceled in making this measurement.) If more than one stroke of the pump is to be made, condensation of vapor in F must be avoided, as otherwise re-vaporization on the down-stroke will leave practically no difference in pressure between E and F. This is easily accomplished by warming the mercury; most of the condensation then takes place in B instead of in F, and when A is closed the down stroke leaves a vacuum in F.

If a mixture of gases is present, it may be analyzed as follows. The total amount of gas is first determined as above; then by suitable manipulation of A and the mercury level, the gas is transferred to D, which is evacuated and contains an absorbent for one component of the mixture. When absorption is complete, the residual gas is pumped back into B and re-measured. D may then be opened, cleaned out, charged with another absorbent, and pumped out; the next constituent is then determined in a similar manner, and so on.

Summary

Description is given of apparatus and method for removal of gases from appreciably volatile liquids.

Some uses, actual and potential, for this device are listed.

Description is given of apparatus and method for pumping off, measuring and analyzing small amounts of gas, in absence or presence of condensable vapors.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

CESIUM SULFATE AS A CONFIRMATORY REAGENT IN THE DETECTION OF ALUMINUM

BY HERMAN YAGODA AND H. M. PARTRIDGE

RECEIVED JUNE 25, 1930 PUBLISHED SEPTEMBER 5, 1930

Cesium salts, because of their unique properties, have long been used as reagents in micro-analytical work and with the increasing demand for salts of this element together with the opening of new ore deposits, it seems certain that much more general use of its interesting properties will result both in qualitative and quantitative analysis.

The familiar aluminum tests which depend on the formation of "Thenard's Blue" or "lakes" with organic dyes are not altogether satisfactory, especially for the average student in qualitative analysis. The formation of a relatively copious precipitate of the insoluble cesium alum, $Cs_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, which contains only 4.75% by weight of aluminum, is on the other hand a simple and decisive test. Its sensitivity will be appreciated when it is recalled that a saturated solution of cesium alum at 0° is 0.00745 M with respect to aluminum ion, and that at 16° this value is but slightly greater, 0.0077 M. Concentrations of aluminum down to 0.1 mg. per cc. are easily and rapidly detected.

Procedure

The supposed aluminum hydroxide, separated in the usual manner from the other Group III metals, is dissolved in 1–5 cc. of hot 3 M sulfuric acid by repeatedly pouring the acid through the filter. (If the precipitate is large, it is more convenient to remove some of it and dissolve in an evaporating dish.) The resulting aluminum sulfate solution is cooled and 0.5–1 cc. of approximately 0.25 M cesium sulfate is added. On scratching the walls of the test-tube with a stirring rod, the dense white cesium alum separates and rapidly settles.

Time Required for Precipitation.—Due to the great tendency of cesium alum solutions to remain supersaturated, the following rough classification has been made

Concn. of Al ion in mg. per cc.	5 and greater	1–5	0.1–1
Time for precipitation	instantaneous	1 minute	3 minutes

Interfering Elements.—Although cesium has a great tendency to form double salts with many elements, only bismuth is likely to be troublesome. In practice this possibility of confusion may be eliminated by adding one drop of concd. hydrochloric acid to a portion of the white precipitate. Warm and add 1 cc. of hydrogen sulfide water. A brown precipitate of bismuth sulfide will indicate the presence of that element. Ferric and chromic alums are much more soluble than the aluminum alum. Beryllium and magnesium do not interfere. The elements lanthanum cerium, praseodymium, neodymium, erbium, yttrium, thorium, zirconium (and probably hafnium) form more soluble double cesium sulfates or form them much more slowly than aluminum.

The authors are indebted to the Maywood Chemical Works for their kind cooperation in this and other work which will be described later.

NEW YORK, N. Y.

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

AN OXIDE OF IODINE, I_2O_2. AN INTERMEDIATE COMPOUND

BY WILLIAM C. BRAY

RECEIVED JULY 8, 1930 PUBLISHED SEPTEMBER 5, 1930

The recent experimental proof by Abel and Hilferding[1] that the reaction between iodate and iodide ions in acid solution, long known as a fifth order reaction,[2] is of the fourth order at a low iodide concentration, has led me to reexamine the series of investigations of Skrabal[3] on the rate of formation of iodate and iodide from iodine and hydroxide ion. Skrabal presented strong evidence that HI_3O and $I_3O_2^-$ exist as intermediate compounds in this reaction, and that HI_3O is a loose addition compound of iodine and hypoiodous acid. He also pictured $I_3O_2^-$ as a similar compound of iodine and iodite ion. The present analysis has led to the conclusion that $H_2I_2O_3$ and I_2O_2 also exist as intermediate compounds, and that $I_3O_2^-$ is really an addition compound of I_2O_2 and iodide ion.

Skrabal succeeded in demonstrating that the results of his rate measurements could be represented by three rate laws, A, B and C, and postulated the following mechanisms

	Relatively rapid equilibrium	$2IOH + I^- \rightleftharpoons I_3OH + OH^-$	(1a)
A	Rate-determining step	$I_3OH \longrightarrow$	(2)
	Main reaction	$3IOH + 3OH^- = 2I^- + IO_3^- + 3H_2O$	
	Relatively rapid equilibrium	$2I_3^- + OH^- \rightleftharpoons I_3OH + 3I^-$	(1b)
B	Rate-determining step	$I_3OH \longrightarrow$	(2)
	Main reaction	$3I_3^- + 6OH^- = IO_3^- + 8I^- + 3H_2O$	
	Relatively rapid equilibrium	$3I_3^- + 4OH^- \rightleftharpoons I_3O_2^- + 6I^- + 2H_2O$	(3b)
C	Rate-determining step	$I_3O_2^- \longrightarrow$	(4)
	4 + rapid steps	$I_3O_2^- + 2OH^- = IO_3^- + 2I^- + H_2O$	(5)
	Main reaction (Sum)	$3I_3^- + 6OH^- = IO_3^- + 8I^- + 3H_2O$	(6)

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[1] Abel and Hilferding, *Z. physik. Chem.*, 136, 186 (1928).

[2] (a) Dushman, *J. Phys. Chem.*, 8, 453 (1904); (b) Skrabal, *Z. Elektrochem.*, 28, 224 (1922); 30, 109 (1924); (c) Abel and Stadler, *Z. physik. Chem.*, **122**, 49 (1926).

[3] Skrabal, (a) *Monatsh.*, **32**, 815–903 (1911); (b) *Oesterr. Chem.-Ztg*, No. 11 (1913); (a) is the fifth paper of a series of twelve, 1907–1916, on hypohalous acids and hypohalites, and (b) is a general discussion of the stoichiometric reactions of iodine isolated and studied in his investigations.

A and B have the same rate-determining step, (2), the disappearance of I_3OH in a first order reaction; they show differences in the rate laws, in the equilibria that precede the rate-determining step, and in the main reactions, merely because the initial concentrations of OH^-, HIO, I^-, I_3^- and I_2 differ in the two sets of experiments. C involves another rate-determining step, (4), the disappearance of $I_3O_2^-$, which is also a first order reaction. This reaction, termed by Skrabal the "slow" reaction, was detected in the presence of B; and, by suitable variation of the experimental conditions, was studied as a limiting reaction.

Additional evidence for this mechanism was presented by Xkrabal by means of rate measurements in the analogous bromine reactions at low concentrations of hydroxide ion.[4] The results furnish for the existence of HBr_3O a proof similar to that for the existence of HI_3O, and show that there is a second independent reaction resembling, but not identical with, that which involves $I_3O_2^-$. Measurements of the rate of formation of chlorate in solutions which contain hypochlorite and hypochlorous acid[5] have given no indication of the existence of either HCl_3O or $Cl_3O_2^-$. There is thus definite evidence that oxyhalogen compounds containing three halogen atoms per molecule exist as intermediate compounds, and that the tendency of such compounds to form decreases rapidly in the order iodine, bromine and chlorine. It will be recalled that the stability of the complex trihalide ions, as I_3^-, Br_3^- and Cl_3^-, decreases in the same order.

The relation of HI_3O and $I_3O_2^-$ to other substances and to each other are shown by the rapidly reversible reactions: 1a, 1b, 3b and the following

$$2I_2 + OH^- \rightleftharpoons HI_3O + I^- \qquad (1c)$$
$$I_2 + HIO \rightleftharpoons HI_3O \qquad (1d)$$
$$3HIO + OH^- \rightleftharpoons I_3O_2^- + 2H_2O \qquad (3a)$$
$$3I_2 + 4OH^- \rightleftharpoons I_3O_2^- + 3I^- + 2H_2O \qquad (3c)$$
$$HI_3O + HIO + 2OH^- \rightleftharpoons I_3O_2^- + I^- + 2H_2O \qquad (3d)$$

The valence (or polar number) of iodine in $I_3O_2^-$ is, on the average, the same as in hypoiodous acid, and that in HI_3O is lower. It is thus probable that in the spontaneous first order reactions, (2) and (4), at least one of the three atoms of iodine is changed to a higher, and one to a lower, valence stage than that of hypoiodite iodine.

Under the conditions of Skrabal's experiments there are two, and only two, paths which lead, through HI_3O and $I_3O_2^-$, respectively, to the formation of iodate and iodide. These two paths are to be regarded as independent, even though HI_3O and $I_3O_2^-$ are in equilibrium with each other as shown in 3d. Consideration of the equilibria, 1a–d, 3a–d and the hydrolysis of iodine

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[4] Skrabal and Weberitsch, *Monatsh.*, 36, 237–256 (1915). This is the tenth paper of the series mentioned in the preceding reference.

[5] (a) Skrabal and Weberitsch, Ref. 4, p. 246; (b) Foerster and Dolch, *Z. Elektrochem.*, 23, 137 (1917).

$$I_2 + H_2O \rightleftharpoons HIO + H^+ + I^- \qquad (7)$$

leads to the conclusion that the rate of iodate formation must become extremely small in acid solutions which contain iodide, and this is in qualitative agreement with experimental results.[6] It is also to be expected that this spontaneous formation of iodate and iodide from HI_3O or $I_3O_2^-$ is impossible whenever the concentrations of IO_3^-, I^- and H^+ are high enough to enable these substances to react with each other. In this connection, Skrabal proved that the path from $I_3O_2^-$ to iodate and iodide is closely related to, if not identical with, that of the fifth order reaction[2] between IO_3^-, I^- and H^+; he proved this by calculating correctly[7] the value of the equilibrium constant of Reaction 6 from the rate laws and specific reaction rates of "C" and the fifth order reaction. Skrabal, however, did not outline a mechanism for either of the first order reactions, (4) and (2).

Several investigators had commented on the fact that all iodate–halide reactions in acid solution are of the fifth order, while the bromate and chlorate reactions are of the fourth order, and at least ones considered a transition to the lower order probable in the case of the IO_3^-–I^-–H^+ reaction. The recent investigation of Abel and Hilferding[1] has demonstrated that this transition is complete at a sufficiently low concentration of iodide ion, about 10^{-8} molal at 25°. They suggest for the mechanism the rate-determining step

$$HIO_3 + HI\ (\text{or } IO_3^- + I^- + 2H^+) \longrightarrow HIO + HIO_2 \qquad (8)$$

followed by the rapid reduction of HIO and HIO_2 to iodine; but they do not refer at all to the mechanism of the fifth order reaction, for which Abel and Stadler[2c] had written the rate-determining step

$$IO_3^- + 2I^- + 2H^+ \longrightarrow (IO_3{\cdot}2I{\cdot}2H)' \longrightarrow 2HIO + IO^- \qquad (9)$$

(where the middle term represents a Bronsted "critical complex"). Abel and Hilferding have thus left open the question as to a connection between the fourth and fifth order reactions.

On considering this question, Dr. Liebhafsky and I have concluded that Reaction 8 cannot be the first step in 9, that complete independence is improbable on account of the similarity and high orders of the two reactions, and that they can be brought into close relationship by assuming as an intermediate compound either $H_2I_2O_3$ or I_2O_2. I have now found this assumption to be consistent with Skrabal's reactions. In the following mechanisms, for reasons which will be explained later, both $H_2I_2O_3$ and I_2O_2 are assumed to exist.

Fourth order reaction at low concentration of iodide.

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[6] (a) Skrabal, Ref. 3b, p. 8; (b) Abel, *Nernst Festschrift*, 1 (1912).

[7] Skrabal, Ref. 3a, pp. 878–881.

[8] Skrabal, Ref. 2b, p. 124 (1924); *Monatsh.*, 36, 230 (1915).

Relatively rapid equilibrium	$IO_3^- + I^- + 2H^+ \rightleftharpoons H_2I_2O_3$	(10a)
Rate-determining step	$H_2I_2O_3 \longrightarrow HIO_2 + HIO$	(11)
Main reaction	$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$	(12a)

Fifth order reaction, with excess iodide.

Relatively rapid equilibrium	$IO_3^- + I^- + 2H^+ \rightleftharpoons H_2I_2O_3 \rightleftharpoons I_2O_2 + H_2O$	(10b)
Rate-determining step	$I_2O_2 + I^- \longrightarrow I_3O_2^-$	(13)
Rapid follow reactions	$I_3O_2^- + 6I^- + 4H^+ = 3I_3^- + 2H_2O$	(14)
Main reaction	$IO_3^- + 8I^- + 6H^+ = 3I_3^- + 3H_2O$	(12b)

There is thus a "forking"[9] at the $H_2I_2O_3$ stage between a first order reaction (11) and a second order reaction which involves iodide ion (13). The rapid follow reactions, of course, take place in steps, which, in (14), are related to the reverse reactions of Nos. 3a–d. One of these, the reverse of **(3a)**

$$I_3O_2^- + H^+ + H_2O \longrightarrow 3HIO \qquad (14a)$$

is of especial interest, since it leads to three molecules of hypoiodite, as postulated in Reaction **9**. **A** consideration of these reactions leads to the conclusion that $I_3O_2^-$ is extremely unstable in an acid iodide solution.

The complete correspondence between the two series of reactions, **10b**–13–14 and **3b–4–5,** shows that, in this path, there is only one rate-determining step between iodine and iodate–iodide, and that Equation 4 may be completed by writing it as the reverse of (13). The assumption that these two rates are equal at equilibrium leads directly to an expression for the equilibrium constant of Reaction 6, closely related to that verified by Skrabal[7]

$$\frac{(IO_3^-)(I^-)^8}{(I_3^-)^3(OH^-)^6} = \frac{k_C}{3k_5k_w^2} \qquad (15)$$

where

$$-d(I_3^-)/dt = 3d(IO_3^-)/dt = k_C(OH^-)^4(I_3^-)^3/(I^-)^6 \qquad (16)$$
$$-d(IO_3^-)/dt = k_5(IO_3^-)(I^-)^2(H^+)^2, \text{ and } K_w = (H^+)(OH^-)$$

In Skrabal's other path from iodine to iodate–iodide there is a single rate-determining step (2), only at a distance from the final equilibrium; a second independent rate-determining step, presumably the reverse of (10), will manifest itself as equilibrium is approached; and the calculation of the equilibrium constant of Reaction 6 from the kinetic data is obviously impossible. The following reactions are suggested to complete (2), and to represent the subsequent relatively rapid steps in the alkaline solution

(Equation 2)	$HI_3O + H_2O \longrightarrow HIO_2 + 2I^- + 2H^+$	(17)
Rapid follow reactions	$2H^+ + 2OH^- = H_2O$	(17a)
	$I_3^- + OH^- = 2HIO + I^-$	(17b)
	$HIO_2 + HIO = H_2I_2O_3$	(17c)
	$H_2I_2O_3 + 2OH^- = IO_3^- + I^- + 2H_2O$	(17d)

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[9] (a) This term was suggested by Luther; Bray, *Z. physik.* Chem., **54, 465** (1906); (b) Skrabal, Ref. 3a, p. 880.

It will be noted that the main reaction (6) is the sum of these reactions and (1b); and that (17c), the reverse of (11), appears as one of the rapid follow reactions. In the reverse case in acid solution, it is doubtful whether the rate-determining step (11) will always be followed by the reverse of (2), since this involves the assumption that HIO_2 cannot be reduced by iodide ion in acid solution by any other path than that through HI_3O. The above mechanism requires the presence of I_3^-, HIO_2 and OH^-, and therefore of I_2 and IO_2^- ion, and is thus at variance with the assumption that $I_3O_2^-$ can be formed rapidly from I_2 and IO_2^-.

It has already been mentioned that Skrabal[4] demonstrated two independent paths in the spontaneous formation of bromate and bromide from bromine in weakly alkaline solution, and concluded for one of them that the decomposition of HBr_3O is the rate-determining step. The reverse reaction between bromate and bromide ions in acid solution is well known to be the fourth order.[10] There is thus a complete analogy with the iodine path through HI_3O, and we may postulate a series of intermediate reactions which corresponds exactly with that presented in the preceding paragraph. The other path requires a more detailed consideration.

Skrabal's rate law[4]

$$-d(Br_3^-)/dt = 3d(BrO_3^-)/dt = k_2(OH^-)^4(Br_3^-)^3/(Br^-)^7 \qquad (18)$$

differs from Equation 16 only in the exponent of the halide term, 7 instead of 6. The rate law for the fourth order reaction is

$$-d(BrO_3^-)/dt = k_4(BrO_3^-)(Br^-)(H^+)^2 \qquad (19)$$

Skrabal demonstrated that the equilibrium constant, K, of the main reaction

$$3Br_3^- + 6OH^- = BrO_3^- + 8Br^- + 3H_2O \qquad (20)$$

can be calculated satisfactorily from an expression equivalent to

$$K = k_2/3k_4K_w^2 \qquad (21)$$

which is identical in form with Equation 15.

This evidence proves as conclusively as is possible that there is only one rate-determining reaction in this path, and that Equations 18 and 19 represent its rates in opposite directions far from equilibrium. The formulas of the bromine compounds involved in this rate-determining reaction are limited to the compositions Br_2O_2 and $H_2Br_2O_3$. We have chosen both of these substances, rather than two isomers of one of them. On this basis the mechanism of Skrabal's reaction, 20, by this path, is as follows

Relatively rapid equilibrium $3Br_3^- + 4OH^- \rightleftharpoons Br_2O_2 + 7Br^- + H_2O$ (22)
Rate-determining step $Br_2O_2 + H_2O \longrightarrow H_2Br_2O_3$ (23)
Rapid follow reaction $H_2Br_2O_3 + 2OH^- = BrO_3^- + Br^- + H_2O$ (24)

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[10] (a) Judson and Walker, J. Chem. *Soc.*, 73, 410 (1898); (b) Skrabal and Weberitsch, *Monatsh.*, 36, 211–256 (1915); (c) Skrabal, *Z.* Elektrochem., 30, 109–124 (1924); (d) Bray and Davis, THIS JOURNAL, 52,1427–1435 (1930).

Similarly, the first stage in the fourth order reaction in acid solution is the relatively rapid equilibrium:

$$BrO_3^- + Br^- + 2H^+ \rightleftharpoons H_2Br_2O_3 \tag{25}$$

which is the reverse of (24) and corresponds exactly with the iodine reaction (10a). The rate-determining step in this path is the reverse of (23); but there is a forking at this stage, and some of the $H_2Br_2O_3$ changes to $HBrO_2 + HBrO$ (cf. the preceding paragraph and Reaction 11).

This close relationship with the corresponding iodine reactions is a striking result. The only difference is in the path with the single rate-determining step, and is shown, for example, by the presence of one more halide in Equilibrium 22 than in (3b). It seems justifiable to conclude that the same transitions $X_3O_2^- \overset{\alpha}{—} X_2O_2 \overset{\beta}{—} H_2X_2O_3$ actually occur in both cases. In the bromine reactions the β step *(23)* is the slower, and $Br_3O_2^-$ may be assumed to be included in (22); while in the iodine reactions the α step (13b) is the slower, and the equilibrium $I_2O_2 + H_2O \rightleftharpoons H_2I_2O_3$ may be assumed to be established relatively rapidly.

The rather complicated argument in favor of the existence of both $H_2I_2O_3$ and I_2O_2 may be restated as follows. Reasons were given for assuming an intermediate step in the fourth order iodate reaction. $H_2I_2O_3$ was chosen because it is directly related to both $HIO_3 + HI$ and $HIO_2 + HIO$. Reasoning by analogy, $H_2Br_2O_3$ was assumed in the exactly similar fourth order bromate reaction. The single rate-determining step in the path between bromate–bromide and bromine was shown to involve a second intermediate compound of similar composition, and Br_2O_2 was chosen. By analogy again, I_2O_2 was concluded to exist in the corresponding path between iodate–iodide and iodine. It is of interest to note that, even if $H_2I_2O_3$ and $H_2Br_2O_3$ are considered to be indefinite critical complexes, the reasoning is unchanged, and I_2O_2 and Br_2O_2 are still to be regarded as definite chemical compounds.

A molecule of I_2O_2 (or Br_2O_2) contains 26 valence electrons, and in the simplest electronic formula corresponding to IOOI or OIIO each of the four atoms has eight electrons associated with it. The formation of an addition compound with I^- or H_2O presents no more difficulty than the formation of I_3^- from I_2 and I^-; in all these cases at least one iodine atom must be associated with more than four pairs of valence electrons. $H_2I_2O_3$ is unsymmetrical, and is more closely related to $H^+ + IO_3^-$ and $H^+ + I^-$ than to HIO_2 and HIO (cf. the relative rates of Reactions 10a and 11). $I_3O_2^-$ undoubtedly reacts very rapidly in acid solution with H^+ and H_2O to form 3HIO (cf. 14a), and there seems to be no evidence that it is directly related to iodine and iodite ion.

The possibility that I_2O_2 might form an addition compound also with iodine was considered. As a result the following mechanism is suggested for the fifth order iodate reaction which is observed in the presence of tri-iodide:

Relatively rapid equilibrium $IO_3^- + I_3^- + 2H^+ \rightleftharpoons I_4O_2 + H_2O$ (26)

Rate-determining step $I_4O_2 + I^- \longrightarrow I_3O_2^- + I_2$ (27)

with rapid follow reactions as in (14). This mechanism is in agreement with the observation of Abel and Hilferding[1] that tri-iodide has no effect on their fourth order reaction (at low iodide concentration); but an additional assumption, that equilibrium in (27) is far to the right, seems necessary in order to explain why Skrabal found no trace of the reverse of (27) in his investigations.[11]

The value of any proposed mechanism must be judged by its usefulness, since a rigid proof is impossible. In the present instance Skrabal's proposals, with the extensions here presented, bring into close relationship the complicated reactions of iodine and of bromine with hydroxide ion and the reverse reactions in acid solution. It is hoped that the suggested or related intermediate compounds will prove useful in future work.

BERKELEY, CALIFORNIA

NOTE

The Atomic Weight of Chlorine. The Solubility of Silver Chloride.—We should like to call attention to the fact that Honigschmid and Chan,[1] in their recent work on the atomic weight of chlorine, have apparently neglected a rather important correction which affects the calculation of the Cl:AgCl ratio. Regarding the silver chloride lost in nephelometric tests, in determining the Cl:Ag ratio, the writers state: "Unter den Fällungsbedingungen enthält die klare eisgekühlte Analysenlösung bei 0° nur etwa 0.05 mg. AgCl pro Liter. Da für jede Nephelometerprobe etwa 50 cm.^{3}, also in ganzen hochstens 150 cm.^{3}, der Lösung entnommen wurden, konote der durch die Probenahme bedingte Verlust an AgCl kaum mehr als 0.01 mg. betragen, war also bei der folgenden Wägung des Chlorsilbers zu vernachlässigen."

Direct nephelometric measurements of the solubility of flocculent silver chloride in pure nitric acid show that the value accepted by Honigschmid and Chan as the solubility of silver chloride at 0° in the saturated analytical liquid at the *end-point* is entirely too low. Such measurements, made in this Laboratory in another connection, have yielded the following data.

Temp., °C.	Molarity of nitric acid	AgCl per liter, g.
0.5	0.00	0.00072
.5	.11	.00090
.5	.24	.00100
.5	.49	.00102
.5	.99	.00105

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[11] Cf. Skrabal, Ref. 3a, p. 877.

[1] Hönigschmid and Chan, *Z. anorg. allgem. Chem.*, 163, 315 (1927).

Although Honigschmid and Chan do not state the concentrations of nitric acid in their analytical solutions, it seems reasonable to estimate that at least 0.001 g. of silver chloride per liter was withdrawn in the nephelometric test portions. It may be pointed out, moreover, that this is a minimum figure, because equilibrium is approached only slowly when these solutions are allowed to stand in an ice-bath. In our measurements, equilibrium was approached from the low-temperature side after completely freezing the solutions.

In order to estimate the error in the calculated atomic weight of chlorine resulting from the omission of the correction for silver chloride lost in nephelometric tests, we have recalculated the results of Honigschmid and Chan's final gravimetric series, assuming a correction of +0.00015 g. of silver chloride in each analysis. The corrected mean of the series, 35.456, differs only a little from the value 35.457 obtained by Honigschmid and Chan. However, since the correction affects only the gravimetric series, we can no longer regard the identical agreement of the gravimetric and nephelometric means, found by the above writers, as having any particular significance. Furthermore, the correction increases considerably the discrepancy in the results of the "complete synthesis" of the silver chloride. This can be seen from the total weights, in grams, corresponding to the eight completed experiments.

	Cl in vac.	Ag in vac.	Cl + Ag	AgCl in vac.	Difference
H. and C.	21.32439	64.88109	86.20548	86.20578	+0.00030
Recalcd.	21.32439	64.88109	86.20548	86.20698	+0.00150

It should be emphasized that the correction in question depends upon the number of nephelometric tests, which in the above case was unusually small. It seems particularly worth while to call attention to the correction because, as far as we are able to determine, it has been overlooked in other recent work from the Munich laboratory.

DEPARTMENT OF CHEMISTRY
THE RICE INSTITUTE
HOUSTON, TEXAS

ARTHUR F. SCOTT
CLYDE R. JOHNSON

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE REACTION BETWEEN CITRONELLAL AND SOME ORGANOMAGNESIUM HALIDES

BY HENRY GILMAN AND W. F. SCHULZ

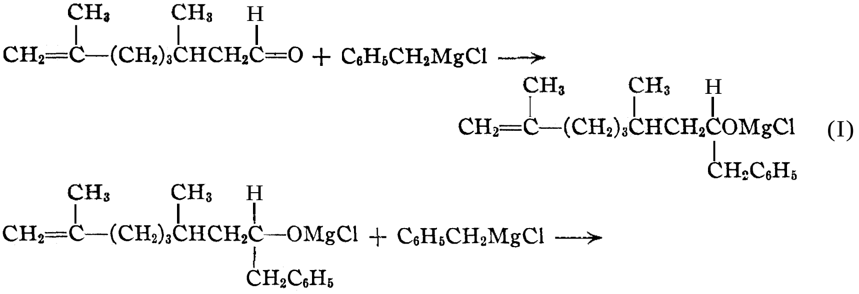
RECEIVED APRIL 28, 1930 PUBLISHED SEPTEMBER 5, 1930

Introduction

A very good case has been made for the non-addition, under usual experimental conditions, of organomagnesium halides to an ethylenic linkage.[1] There is, however, an apparent addition to such a linkage in compounds having the olefinic bond conjugated with another, and a different double bond, such as the carbonyl group in benzalacetophenone, $C_6H_5CH{=}CH\text{-}COC_6H_5$. Kohler and co-workers have demonstrated in an unequivocal manner that such conjugated systems can undergo 1,4-addition with the Grignard reagent. The enolic compound obtained subsequent to hydrolysis of the 1,4-addition intermediate then rearranges to give as an ultimate product a compound which might have been interpreted (and was interpreted incorrectly by earlier investigators) as involving direct addition to the ethylenic linkage.

The author of a recent book on organomagnesium halides,[2] in emphasizing the probability of direct addition to an ethylenic linkage, directs attention to a study by Rupe[3] on the purported addition of benzylmagnesium chloride to the ethylenic linkage in citronellal and makes the pointed observation that in this compound "1,4-addition is absolutely excluded."

The following reactions illustrate Rupe's interpretation of the mechanism of reaction.



$$\mathrm{CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}(CH_2)_3\overset{CH_3}{\overset{|}{C}}HCH_2\overset{H}{\overset{|}{C}}{=}O + C_6H_5CH_2MgCl \longrightarrow}$$

$$\mathrm{CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}(CH_2)_3\overset{CH_3}{\overset{|}{C}}HCH_2\underset{CH_2C_6H_5}{\underset{|}{\overset{H}{\overset{|}{C}}}}OMgCl} \qquad \text{(I)}$$

$$\mathrm{CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}(CH_2)_3\overset{CH_3}{\overset{|}{C}}HCH_2\underset{CH_2C_6H_5}{\underset{|}{\overset{H}{\overset{|}{C}}}}{-}OMgCl + C_6H_5CH_2MgCl \longrightarrow}$$

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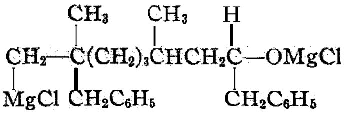
[1] Gilman and Harris, *Rec. trav. chim.*, 49, June, (1930). References to earlier studies may be traced from this article.

[2] Courtot, "Le Magnésium en Chimie Organique," published in 1926 by the author at Nancy (see pages 317 and 324).

[3] Rupe, *Ann.*, 402, 161 (1914). The present controversy on the constitution of citronellal does not affect the discussion in our paper because neither the double bond in the methylene form nor the double bond in the isopropylidene form is conjugated with the carbonyl group.

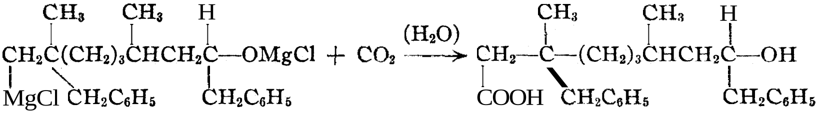


$$\underset{\mathrm{MgCl}}{\mathrm{CH_2}}\!-\!\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_2C_6H_5}}{\mathrm{C}}}\mathrm{(CH_2)_3}\overset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{HCH_2}\overset{\mathrm{H}}{\underset{\mathrm{CH_2C_6H_5}}{\mathrm{C}}}\!-\!\mathrm{OMgCl} \quad \text{(II)}$$

(A)

It appeared highly improbable from our earlier studies[1] that addition had occurred as postulated by Rupe in Reaction II. The results of this study show that there has been no addition to the ethylenic linkage. This has been established by indirect methods.

If addition had taken place in accordance with Reaction II, then a new Grignard reagent should result. This organomagnesium chloride having the terminal group $—CH_2MgCl$ would be expected to react essentially like other compounds having the $—CMgX$ group, and on carbonation, for example, should give the corresponding carboxylic acid.



$$\underset{\mathrm{MgCl}}{\mathrm{CH_2}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_2C_6H_5}}{\mathrm{C}}}\mathrm{(CH_2)_3}\overset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{HCH_2}\overset{\mathrm{H}}{\underset{\mathrm{CH_2C_6H_5}}{\mathrm{C}}}\!-\!\mathrm{OMgCl} + \mathrm{CO_2} \xrightarrow{\mathrm{(H_2O)}} \underset{\mathrm{COOH}}{\mathrm{CH_2}}\!-\!\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_2C_6H_5}}{\mathrm{C}}}\!-\!\mathrm{(CH_2)_3}\overset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{HCH_2}\overset{\mathrm{H}}{\underset{\mathrm{CH_2C_6H_5}}{\mathrm{C}}}\!-\!\mathrm{OH} \quad \text{(III)}$$

(B)

The absence of this carboxylic acid was established in a reaction involving citronellal and three equivalents of benzylmagnesium chloride. This excess of Grignard reagent left one equivalent of benzylmagnesium chloride over and above that required by Reactions I and II. On carbonating the entire reaction mixture, the excess of benzylmagnesium chloride should be converted to the corresponding phenylacetic acid, $C_6H_5CH_2COOH$. If Reaction II took place, then subsequent to carbonation, hydrolysis and extraction with alkali a mixture of acid (B) (from Reaction III) and phenylacetic acid should result. The only acid obtained, however, was pure phenylacetic acid. The purity of the acid was established by determinations of melting point, mixed melting point and neutralization equivalent. We also showed, in like manner, that phenylmagnesium bromide and n-butylmagnesium bromide did not add to the ethylenic linkage, although it should be stated that of the Grignard reagents studied by Rupe only benzylmagnesium chloride was said to have added to the ethylenic linkage.[4]

Objections can be raised against this indirect proof. First, addition may have occurred at the ethylenic linkage, prior to addition to the carbonyl group, and the aldehydo-Grignard reagent formed in this manner might then have undergone intramolecular reaction to give a cyclic *sec*ondary alcohol. This is altogether unreasonable when one considers that aldehydes react almost instantly with Grignard reagents,[5] and that there is

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[4] Rupe (Ref. 3, footnote on p. 161) has remarked that "benzylmagnesium chloride has a great tendency to 1,2-addition to a double bond." No such tendency was noted in a comprehensive study by Gilman and McGlumphy, *Rec. trav. chim.*, 47, 418 (1928).

[5] Gilman, Heck and St. John, *ibid.*, 49, 212 (1930). Obviously aldehydes with high

not, up to the present time, any case of even a slow addition of RMgX compounds to a non-conjugated ethylenic linkage.[6] Second, the acid (B) might actually have been formed in accordance with Reactions II and III and yet not revealed itself in the alkali extraction because of intramolecular esterification to give a ten-membered lactone. This also is highly unlikely per se, and particularly under our experimental conditions, because the lactone even though formed quantitatively should have been hydrolyzed in part, at least, by the alkali treatment to give the acid (B). This acid might subsequently have been converted to lactone, in part. Either or both of these products should have revealed themselves as impurities in the phenylacetic acid, but the high purity of this acid belied admixture, in any significant quantity, of contaminating lactone or acid.

Experimental Part

A solution of 23.1 g. (0.15 mole) of citronellal in 50 cc. of ether was added dropwise to a well-stirred solution containing 0.45 mole of benzylmagnesium chloride in 250 cc. of ether. Stirring and gentle refluxing were continued for fifteen minutes after addition of the aldehyde. The reaction mixture was then carbonated in a customary manner,[7] poured into iced dilute sulfuric acid, and the ether layer separated, washed with water and extracted with 10% sodium hydroxide. The alkaline extract was washed with ether, acidified with hydrochloric acid, and the precipitate so obtained filtered, washed with a minimum of water and dried in the air. Its melting point and mixed melting point with phenylacetic acid were identical with that of phenylacetic acid. The neutralization equivalent was 137.1, and the calculated value for phenylacetic acid is 136.1.

The reaction undoubtedly proceeded in accordance with that carried out by Rupe[3] because we also obtained the oil described by him (the product from hydrolysis of compound (A) in Reaction II) and its boiling point (244°/9 mm.) agreed with that determined by him. We have not investigated the constitution of this compound.

In a corresponding experiment with phenylmagnesium bromide the benzoic acid obtained melted at the correct melting point for this acid and showed no depression in a mixed melting point determination with an authentic specimen. The neutralization equivalent was 121.2, and the calculated equivalent for benzoic acid is 122.

The n-valeric acid obtained from a similar reaction between citronellal and an excess of n-butylmagnesium bromide had the following constants: b. p. 186°; d^{20}_{20} 0.9362; n^{20}_{α}, 1.404; and its neutralization equivalent was 108.8 (calcd. 102.1).

Summary

Contrary to the interpretations of others, benzylmagnesium chloride does not add to the ethylenic linkage in citronellal.

AMES, IOWA

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steric hindrance about the carbonyl group will react more slowly than aldehydes without such steric hindrance.

[6] An interesting case of 1,4-addition to a conjugated system that is part aliphatic and part aromatic has been described recently by Gilman, Ruby and Kinney, THIS JOURNAL, 51, 2252 (1929). There is a somewhat remote possibility that even though there is no formal conjugated system in citronellal, there still might be addition to a conjugated system resulting from the spatial contiguity of the aldehyde and ethylenic groups.

[7] Gilman and Parker, *ibid.*, 46, 2816 (1924).

[CONTRIBUTION FROM THE SWAN-MYERS COMPANY]

CHEMICAL STUDIES ON POLLEN AND POLLEN EXTRACTS
I. DISTRIBUTION OF NITROGEN EXTRACTED BY VARIOUS SOLVENTS

BY EDMOND E. MOORE AND MARJORIE B. MOORE

RECEIVED APRIL 30, 1930 PUBLISHED SEPTEMBER 5, 1930

Whether one is inclined to accept or to reject the theory that pollen sensitization or allergy is an anaphylactic phenomenon due to one or more specific proteins of the pollen, it is evident that a careful chemical study of different pollens is desirable as a basis for further research which may lead to the isolation of the actual causative agent or agents.

The literature yields only very limited information on the subject of pollen composition. As proteins are usually considered to be the offending agents in cases of allergy, it seemed desirable to begin such a study by determining the nitrogen extractable by various solvents.

Heyl,[1,2] Caulfeild, Cohen and Eadie,[3] Koessler[4] and Csonka, Bernton and Jones[5] have contributed valuable information on this subject. However, because of the varying methods of attack the results of the different investigators do not agree.

Certain definitions which have been made to fit the animal proteins cannot be applied to vegetable proteins. This fact must be kept in mind by anyone who works with the proteins of pollen. In this work the purpose was to extract the pollen with different solvents in such a manner as to cause the least possible denaturation. No heat or concentrated solutions of electrolytes were used. The development by Koch and McMeekin[6] of a satisfactory direct colorimetric micro-analysis for nitrogen has made it possible to determine nitrogen in pollen and pollen fractions with greater ease and accuracy than could be secured by any macro method.

For this work four pollens have been chosen; two representative of the type causing spring hay fever, timothy (*Phleum pratense* L.) and orchard grass (*Dactylis glomerata* L.) and two of the type causing autumnal hay fever, short ragweed (*Ambrosia elatior* L.) and giant ragweed (*Ambrosia trifida* L.).

[1] F. W. Heyl, "Analysis of Ragweed Pollen," THIS JOURNAL, 39, 1470–1476 (1917).

[2] F. W. Heyl, "Analysis of Ragweed Pollen," *ibid.*, 41, 670–685 (1919).

[3] A. H. W. Caulfeild, C. Cohen and G. S. Eadie, "The Antigenic Properties of Pollen Fractions," J. *Immunology,* 12, 153–175 (1926).

[4] J. H. Koessler, "Studies on Pollen and Pollen Diseases. I. The Chemical Composition of Ragweed Pollen," *J. Biol. Chem.*, 35, 415–434 (1918).

[5] F. A. Csonka, H. S. Bernton and D. B. Jones, "Proteins of Timothy and Orchard Grass Pollen and their Relation to Vernal Hay Fever," *Proc. Soc. Exptl. Biol. Med.*. 23, 14–16 (1925).

[6] F. C. Koch and T. L. McMeekin, "A New Direct Nesslerization Micro-Kjeldahl Method and a Modification of the Nessler–Folin Reagent for Ammonia," THIS JOURNAL, 46, 2066–2069 (1924).

Small samples (*i. e.*, two to four grams) of pollen were used. This obviated the necessity of handling large volumes of solutions when exhaustive extraction was attempted. The nitrogen determination by the modified micro-Kjeldahl method of Koch and McMeekin[6] permitted accurate estimation of the nitrogen in these solutions.

Extractions were made of at least four samples of each pollen studied. Preliminary work had shown the amount of solvent necessary for practically complete extraction with each extracting menstruum.

All water used was redistilled from alkaline permanganate and tested for ammonia.

Method

An accurately weighed sample of *dry* pollen, usually two or four grams, was placed in a dry beaker. A suitable portion of ether was then added and mixed with the pollen sample. The mixture was filtered by suction through a hardened paper in a **4.5-cm.** Biichner funnel. The residue was washed with a little ether and again carefully transferred to the beaker to be re-extracted. Previous work had shown that it was possible to determine the completeness of extraction by the color imparted by the residue to the fresh ether. The ragweed pollens required a greater number of ether extractions than did the grass pollens, the total volume of ether solution being for the ragweeds **100** cc. and for the grasses **50** cc.

The same method was used in carrying out the other extractions upon the ether-extracted samples, the residue from filtration being transferred back to the beaker for mixing with fresh portions of the solvent. The volumes of each extract obtained, using four-gram samples, were: water, **250** cc.; salt solution (**10%** sodium chloride at **60°**), usually **100** cc.; alcohol solution (75%), **100** cc.; alkaline solution (**0.2%** sodium hydroxide), usually **100** cc.

Nitrogen was determined on 5- or **10-cc.** aliquots of each of these extracts and on weighed samples (preferably **20** to **30** mg.) of the original dry pollen and of the residue which had been thoroughly washed with water to remove alkali and dried in air and over sulfuric acid. In the case of the grass pollens, enormous swelling took place in the alkaline solution and the residue finally obtained, even after repeated washings with

TABLE I

NITROGEN DISTRIBUTION

	Fraction	Giant ragweed	Short ragweed	Orchard grass	Timothy
	Whole pollen	**4.36**	**4.26**	**4.37**	**4.92**
(A)	Ether-soluble	**0.079**	**0.053**	**0.005**	**0.003**
(B)	Water-soluble	**1.31**	**1.315**	**1.38**	**1.49**
	(1) Rptd. by dialysis	**0.074**	**0.125**	**0.021**	**0.173**
	(2) **In** filt. from dialysis	.053	.094	.031	.19
(C)	Salt-soluble (**10%** NaCl)	**.48**	.354	**.23**	.705
	(1) Rptd. by dialysis	.013	.013	.016	.064
	(2) In filt. from dialysis	**.02**	.042	.021	**.05**
(D)	Alcohol-soluble (**75%** EtOH)	.345	**.30**	.029	.035
(E)	Alkali-soluble (**0.2%** NaOH)	.118	.135	**.26**	**.50**
	(1) Rpt. by acid	.065	**.05**	.053	**.19**
(F)	Residual **N**	**1.98**	**2.18**	**2.48**	**1.89**
	Total	**4.31**	**4.34**	**4.38**	**4.62**

water, formed a hard cake on drying, probably due to incomplete removal of the alkali. The ragweed pollens gave residues which were easily powdered.

Aliquots of 100 and 50 cc., respectively, of the water and of the salt extracts were used for dialysis. They were electrodialyzed under toluene in gold beaters' sacs at about 2° for approximately a week. The distilled water outside the sacs was frequently changed. Carbon electrodes with a potential difference of 110 volts were used. In the case of the salt extract a preliminary dialysis was necessary in order to remove the excess sodium chloride before electrodialysis

Precipitates were formed by electrodialysis of both water and salt extracts. These were separated from the solutions by centrifugation. Nitrogen was determined on these precipitates and on aliquots of the solutions.

Table I and the figures give the results obtained. The values for nitrogen are all calculated on the basis of the original dry pollen.

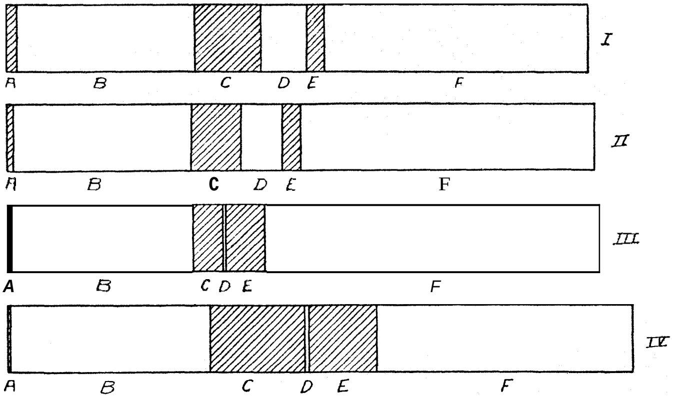

Fig. 1.—Nitrogen extracted. I, Giant ragweed; II, short ragweed; III, orchard grass; IV, timothy. A, by ether; B, by water; C, by sodium chloride solution; D, by ethyl alcohol solution; E, by sodium hydroxide solution; F, in residue.

Discussion

Only a very small amount of nitrogen was extracted by ether, and this is probably non-protein in nature. However, recent work by Milford[7] indicates that this fraction may be of allergic importance. Although by far the largest part of the nitrogen extractable by the solvents used appeared in the water solution, only a small percentage of this was non-dialyzable under the conditions of these experiments. This may be taken to mean that most of the nitrogen thus extracted is not protein nitrogen. It has been suggested that much of the nitrogen present in the pollen may occur in the form of water-soluble diffusible bases such as betaines. It is also conceivable that enzymes contained in the pollen may have been able to hydrolyze the proteins and change their nitrogen into a dialyzable form

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[7] Edgar L. Milford, "Specific Studies in Allergy. I. The Specific Activity of Pollen Oil," J. *Allergy,* 1, 331–333 (1930).

during the prolonged dialysis. The former theory is supported by the results of Heyl,[2] who found the total coagulable protein plus material precipitated by saturation with zinc sulfate to represent only a small portion of the nitrogen extractable by water. It might be assumed that the action of enzymes mould be greatly retarded by the low temperature and the toluene used in the dialysis. However, because of the large number of enzymes found in pollen (Paton[8]) and because of the small amount of investigation that has been done on them, it would seem unwise to make any assumptions as to their action.

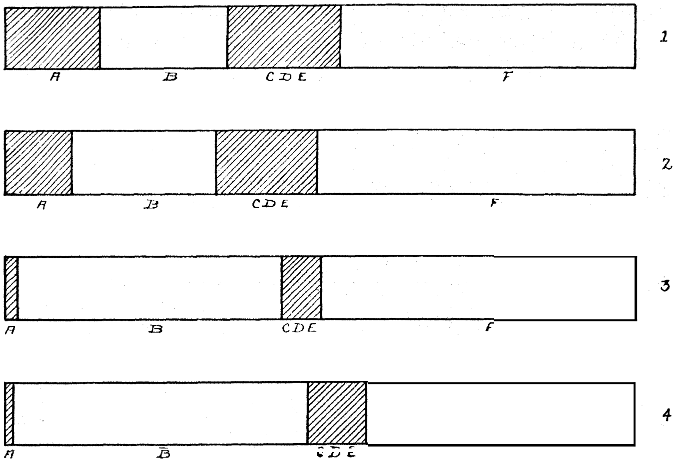

Fig. 2.—Total solids extracted. 1, Giant ragweed; 2, short ragweed; 3, orchard grass; 4, timothy. A, By ether; B, by water; CDE, by sodium chloride, ethyl alcohol and sodium hydroxide; F, in residue.

It is of interest to note that in every case about one-half of the non-dialyzable nitrogen of the water extract is precipitated by dialysis. This behavior would not be expected if the water extract contains only albumin and proteose, as is generally assumed. On the basis of Osborne's[9] definition, this precipitable material should be classified as a globulin. It might be postulated that the albumin has been denatured by continued contact with pure water, but it seems more logical in the present state of our knowledge to assume that most of the globulin present can be extracted by redistilled water with the aid of salts present in the pollen itself.

The nitrogen extracted by salt solution (10% NaCl) is small in amount and a considerable portion of it is dialyzable. The same argument as to

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[8] Julia B. Paton, "Enzymes of Pollen," *Proc. Soc. Exptl. Biol. Med.*, **17**, 60-61 (1919).

[9] Thos. B. Osborne, "The Vegetable Proteins," Longmans, Green and Company, New York, 1924, p. 18.

whether or not this is due to enzyme action applies here as in the water extract. The precipitate may be safely classified as globulin. The fractions soluble in water and diluted salt solutions are generally conceded to be the most important ones as causative agents in allergic conditions.

The alcohol solution (75% EtOH) extracts a small amount of nitrogen. No further work was done on this fraction to determine whether this nitrogen is protein in nature. Clinical studies by various investigators have shown some allergic activity in the alcohol-soluble material from pollens.

A further small amount of nitrogen is extracted by dilute alkali (0.2% NaOH) of which approximately half is precipitated by acidification of the extract. This precipitated material is probably a glutelin, and its importance as a factor in allergy is doubtful.

Approximately half of the nitrogen originally present in the pollen remains in the residue after extraction with all the above solvents. Its nature is not known but as it appears highly probable that the toxic agent in allergic conditions is one easily extracted by body fluids, it may be assumed that this nitrogen is not of clinical importance.

The allergic properties of the various fractions are being studied. No significant difference was found in the amount of nitrogen extracted from different pollens by the solvents used.

A difference between the ragweed arid grass pollens is shown in the quantities of material extracted by ether and by water. Table II shows the total solids extracted by ether and by water, and the weight of material left after extraction by all of the solvents mentioned above. These percentages are calculated on the basis of the original dry pollen.

TABLE II

TOTAL SOLIDS

	Giant ragweed	Short ragweed	Orchsrd grass	Timothy
Ether-soluble	**15.4**	**11.1**	**1 9**	**1 6**
Water-soluble	**20.7**	**22.9**	**42.5**	**47.0**
Residual	**46.3**	**49.8**	**49 6**	**42.7**
Soluble in 10% NaCl, 75% EtOH and 0.2% NaOH (by difference)	17.6	16.2	6.0	8.7

Summary

Pollens of giant ragweed (*Ambrosia trifida* L.), short ragweed (*Ambrosia elatior* L.), timothy (*Phleum pratense* L.) and orchard grass (*Dactylis glomerata* L.) were exhaustively extracted with ether, water, salt solution, alcohol and alkali in the order named. Nitrogen was determined on each of these extracts and on the original pollen and the residue.

The water and salt solution extracts were dialyzed. In both dialyses a precipitate was thrown down. Nitrogen was determined in the precipitate and in the filtrate which remained in the dialyzing sac.

The total materials extracted by the ether and by the water were determined as well as the amount of residue remaining. The quantity of material extracted by the combined salt, alcohol and alkali extractions was calculated by difference.

The similarity between the two grass pollens and between the two ragweed pollens is very marked. The grass pollens swelled greatly in alkali while the ragweed pollens did not. The ragweed pollens contain much more ether-soluble material, but only approximately half as much material extractable by water.

The differences in nitrogen content in the similar fractions of the different pollens do not appear to be significant. About half of the nitrogen was not extractable by the solvents used.

The results on the water extracts indicate that most of the nitrogen extracted by this solvent is non-protein. It also appears that the water extract contains globulin.

INDIANAPOLIS, INDIANA

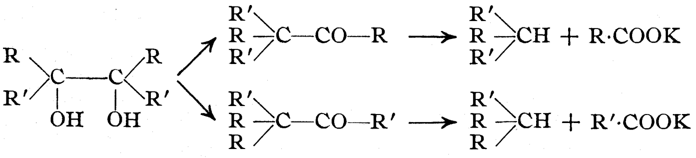
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE EFFECT OF SUBSTITUENTS UPON THE REARRANGEMENT OF BENZOPINACOL

BY JOHN C. BAILAR, JR.

RECEIVED APRIL 30, 1930 PUBLISHED SEPTEMBER 5, 1930

The relative migratory tendencies of organic radicals have often been determined by means of molecular rearrangements. Any rearrangement in which two groups occupy identical positions and are equally free to move might theoretically be used for this purpose, but if the two groups are nearly equal in migratory tendency, each will migrate to some extent, and a mixture of two isomeric products will be formed. The separation of these, or a determination of the relative amounts in which they are present, is often difficult. In the case of the pinacol rearrangement, however, each of the two pinacolones which are formed may be split by the action of alcoholic potassium hydroxide into a hydrocarbon and the potassium salt of an acid. These acids are often readily separated.



Thus Montagne has determined the relative migratory tendencies of the *p*-chlorophenyl and phenyl groups[1] and the *p*-bromophenyl and

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[1] Montagne, *Rec. trav. chim.*, **26**, 253 (1907).

phenyl groups,[2] separating the substituted and unsubstituted acids by the difference in their solubilities. In like manner Gomberg and Bachmann[3] compared the *p*-biphenyl and phenyl groups, and Gomberg and Bailar[4] have compared the *p*-biphenyl group with the *m*- and *p*-bromophenyl groups, separating the acids by the difference in the solubility of the barium salts.

But in many cases a quantitative separation of the acids or their salts is a long and tedious process. The comparisons reported in this article have been made possible by the use of a method which depends upon the determination of the equivalent weight of the mixture of the acids formed from the pinacolones. Knowing this, and the equivalent weight of the two acids which might possibly be present, it is easy to calculate the percentage composition of the mixture, and from this the relative migratory tendencies of the two groups. The equivalent weight of the mixture is determined by titration of a weighed sample with a standard base. The method is not an extremely accurate one, but repeated and careful experiments have shown that the composition of the mixture can be calculated within 5%, even when the two acids are as similar as benzoic and toluic acids.

Experimental

During the course of this investigation ten symmetrically substituted benzopinacols have been subjected to rearrangement. None of these pinacols has been described in the literature. Table I gives the formulas, melting points and analytical data for these, and also ratios indicating the comparative migratory tendencies of the various groups.

The 4,4′-dimethoxy-di-α-naphthyl pinacol was prepared by the action of α-naphthylmagnesium bromide upon anisil; the *sym.*-2,2′- and 3,3′-dimethoxybenzopinacols by reduction of the corresponding ketones by zinc and acetic acid. In the course of preparation of 3-methoxybenzophenone two compounds not previously described were obtained. 3-Methoxybenzoic acid was converted through the chloride into the amide, and thus into the cyanide. This, by treatment with phenylmagnesium bromide, gave the ketone in good yield.

Amide.—White crystals melting at 130°. Anal. Calcd. for $C_8H_9O_2N$: C, 63.54; H, 6.00. Found: C, 63.79; H, 6.11.

Cyanide.—Colorless liquid boiling at 140° at 34 mm. pressure. Anal. Calcd. for C_8H_7ON: C, 72.14; H, 5.30. Found: C, 71.97; H, 5.15.

All of the other pinacols were prepared from the corresponding ketones by the method of Gomberg and Bachmann.[3] In every case the yield of crude pinacol was practically quantitative; in some cases large losses were incurred during the process of purification. Bachmann and Shankland have previously encountered this difficulty.[5]

Two of the ketones used were not known previously. 4-Isopropylbenzophenone

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[2] Montagne, *Rec. trav. chim.*, 29, 154 (1910).

[3] Gomberg and Bachmann, THIS JOURNAL, 49, 236 (1927).

[4] Gomberg and Bailar, *ibid.*, 51, 2236 (1929).

[5] Bachmann and Shankland, *ibid.*, 51,306 (1929).

TABLE I
CONSTANTS AND ANALYTICAL DATA

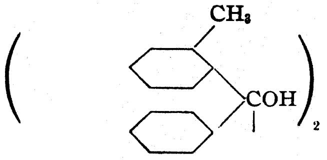
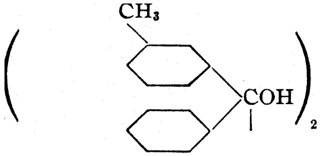
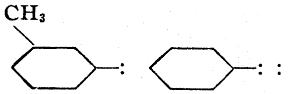
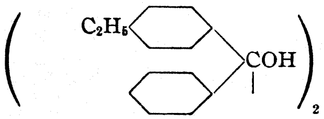
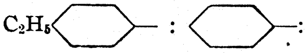
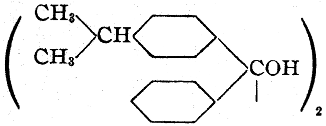
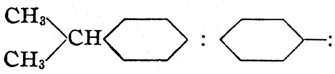
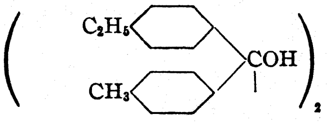
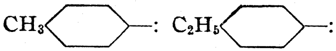
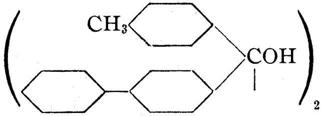
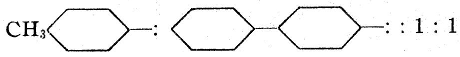
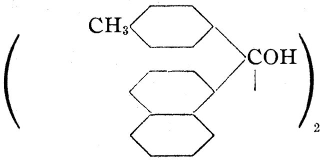
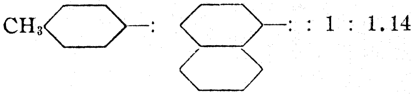
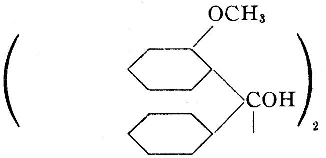
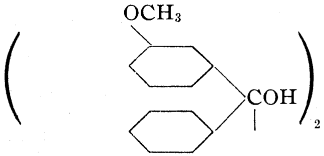
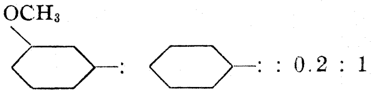
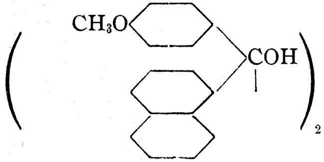
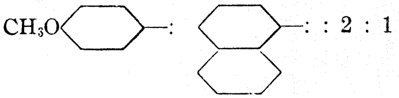
Formula	M. p., °C.	Calcd.	Found	Ratio of migratory tendencies
	156	C, 85.23 H, 6.65	85.09 6.51	No rearrangement
	147–148	C, 85.23 H, 6.65	85.18 6.93	 : : 0.6 : 1
	162–163	C, 85.25 H, 7.16	85.28 6.93	 : : 5 : 1
	161–162	C, 85.28 H, 7.61	85.35 7.41	 : : 9 : 1
	155–156	C, 85.28 H, 7.61	85.02 7.33	 : : 3 : 1

TABLE I (Con luded)

Formula	M. p., °C.	Calcd.	Found	Ratio of migratory tendencies
	175–176	C, 87.87 H, 6.28	87.94 6.11	
	150	C, 87.41 H, 6.12	87.60 5.85	
	168–169	C, 78.83 H, 6.15	78.89 5.98	No rearrangement
	139–141	C, 78.83 H, 6.15	78.54 6.19	
	143–144	C, 82.09 H, 5.75	81.91 5.61	

was obtained by the reaction of benzoyl chloride and isopropylbenzene; yield, 75%. The best yield is obtained when a large excess of isopropylbenzene is used. The ketone is a colorless liquid which does not crystallize at −10°; b. p. 197° at 10 mm.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.66; H, 7.19. Found: C, 85.44; H, 7.15.

4-Methyl-4'-ethylbenzophenone resulted from the reaction of toluyl chloride and ethylbenzene; yield, 70%. The ketone did not crystallize; b. p. 215° at 10 mm.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.66; H, 7.19. Found: C, 85.49; H, 7.05.

The determination of the migratory tendencies was made as follows. A 3-g. sample of pure pinacol was subjected to rearrangement by boiling with 30 cc. of glacial acetic acid and a small crystal of iodine for one hour. The solution was poured into 400 cc. of water containing a pinch of sodium bisulfite to remove the iodine. The white precipitate of pinacolone was separated from the liquid by filtration, washed with water and allowed to dry, after which it was boiled with 1 g. of potassium hydroxide in 50 cc. of absolute alcohol for twelve hours. (Two or three hours' boiling suffices to split some pinacolones, but not all of them.) Sometimes the solution turned brown during this boiling; in such cases, the results of the experiments were never concordant, and were discarded. The alcoholic solution was poured into water and evaporated until the precipitate had coagulated. This was then filtered off and the filtrate, which contained the potassium salts of the acids, was extracted with ether in order to remove any remaining traces of foreign organic matter. Upon acidification of the solution, the acids precipitated, and were extracted with ether. The extract was dried over anhydrous sodium sulfate, filtered and allowed to evaporate. The residue was weighed and after being dissolved in alcohol, was titrated with standard sodium hydroxide. The results obtained in the three experiments which were carried out with 4,4′-di-isopropylbenzopinacol are shown in Table II. The average of the three values obtained for the ratio of the migratory tendencies of the substituted and unsubstituted groups is 8.9:1. In Table I this is recorded as 9:1; similarly in other cases, realizing that the method is not one of extreme accuracy, we have taken approximate, simple ratios. The approximation did not require as great a change in any other cases as in this one.

TABLE II

EXPERIMENTAL DATA

	Weight of mixed acids	Cc. of 0.1852 *N* NaOH	Equivalent weight of mixture	Weight percentage of benzoic acid	Mole percentage of benzoic acid	Migratory tendency
1	0.6024	25.22	128.99	87.75	90.34	9.3:1
2	.5948	25.16	127.64	86.67	89.74	8.7:1
3	.4590	19.42	127.64	86.67	89.74	8.7:1

In the case of 4,4′-di-isopropylbenzopinacol one of the pinacolones was formed in so much greater quantity than the other that separation of the two was easy. Three recrystallizations from glacial acetic acid gave pure benzoyl-4,4′-di-isopropyltriphenylmethane; m. p. 140°.

Anal. Calcd. for $C_{32}H_{32}O$: C, 88.52; H, 7.67. Pound: C, 88.72; H, 7.47.

This pinacolone, heated with alcoholic potassium hydroxide, gave a quantitative yield of 4,4′-di-isopropyltriphenylmethane. This hydrocarbon resisted all attempts at crystallization. In an ice–salt mixture it solidified to a glassy mass.

Anal. Calcd. for $C_{25}H_{28}$: C, 91.40; H, 8.60. Found: C, 91.61; H, 8.77.

Two of the pinacols—those in which the methyl and methoxy groups occupy the ortho-positions—did not rearrange upon boiling for one hour with glacial acetic acid and iodine. Even four hours' boiling had no effect. Heating for two hours with glacial acetic acid and acetyl chloride (a method often used to effect the rearrangement of pinacols) produced no change—longer heating decomposed the pinacols to a sticky mass of unidentifiable products.

Discussion

Thorner and Acree[6] have reported that in the rearrangement of *sym.*-4,4′-dimethylbenzopinacol only the substituted group moves. This indicates that the *p*-tolyl group has such a large migratory tendency in comparison with that of the phenyl group that no definite comparison can be made between the two. It should be possible to assign a definite value to the migratory tendency of the p-tolyl group by comparing it with some other group of large, but known, migratory tendency. Such is the p-biphenyl group, which Gomberg and Bachmann[3] have shown to have a migratory tendency 12.5 times as great as that of the phenyl group. The rearrangement of symmetrical 4,4′,4″,4‴-dimethyldiphenylbenzopinacol shows the p-tolyl and *p*-biphenyl groups to have approximately equal migratory tendencies (Table I). In making this determination we not only determined the equivalent weight of the mixed acids, as outlined above, but we separated the two acids by dissolving the toluic acid out of the mixture with boiling water, in which *p*-phenylbenzoic acid is insoluble. The two methods gave the same result. The relation between the migratory tendencies of the p-tolyl group and the phenyl group has been confirmed by another indirect comparison. The substitution of an ethyl group increases the migratory tendency of the phenyl group five-fold; the rearrangement of symmetrical 4,4′,4″,4‴-dimethyldiethylbenzopinacol shows that a methyl group in the para-position has three times the effect of an ethyl group. Prom this it may be inferred that the p-tolyl radical has a migratory tendency approximately fifteen times as great as the phenyl. A direct comparison of the two is difficult because of the great similarity in their properties and equivalent weights.

The substitution of a methyl radical in the meta-position decreases the migratory tendency of the phenyl radical somewhat; if the substitution is made in the ortho-position, the migratory tendency becomes very small indeed. Not only does the substituted group fail to migrate—it prevents the migration of the unsubstituted group as well. Such a result was not wholly unexpected—Koopal[7] has reported that benzopinacol in which a chlorine or bromine atom has been substituted in the ortho-position rearranges only very slowly—when rearrangement does take place, it is due entirely to the migration of the unsubstituted group. According to Lagrave[8] this inhibition of the rearrangement can be ex-

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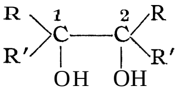
[6] Thorner, *Ber.*, **9**, 482, 1738 (1876); Ann., **189**, 110 (1877); Acree, Am. Chem. J., 33, 190 (1905).

[7] Koopal, *Rec. trav. chim.*, *34*, 134 (1915).

[8] Lagrave, Ann. *chim.*, [10] 8,363 (1927).

plained in the following way. Upon rearrangement of a pinacol, one or the other of the radicals attached to one of the central carbon atoms (C 2) migrates to the other central carbon atom (C 1), but if C 1 is already holding groups of large affinity capacity, it will be unable to accept another group. Such is the case here; the o-tolyl group absorbs so much of the energy of C 1 that very little is left to attract another group from C 2. Hence no rearrangement takes place.



Tiffeneau and Orekhoff[9] have shown that the *p*-anisyl radical migrates exclusively in the rearrangement of 4,4′-dimethoxybenzopinacol. As is shown in Table I, the m-anisyl radical has but one-fifth of the migratory tendency of the unsubstituted phenyl group, and the presence of the methoxy group in the ortho position prevents any rearrangement. The p-anisyl group has twice the migratory tendency of the a-naphthyl group, which in turn is somewhat larger than that of the *p*-tolyl group. The ratio of the migratory tendencies of the *p*-anisyl and phenyl groups is, therefore, in the neighborhood of 40:1.

It will be noticed that the p-anisyl group has a much greater tendency to migrate than the m-anisyl, which, however, is still more prone to migrate than the o-anisyl. The same is true, though less marked, if the substituent is the methyl radical instead of the methoxy. It is apparently true also when the substituent is either a chlorine or a bromine atom.[1,7]

The p-isopropylphenyl group has nine times the migratory tendency of the unsubstituted phenyl radical. Thus the effect of the *p*-isopropyl group is not as large as that of the *p*-methyl, but is much larger than that of the p-ethyl. Whether this peculiarity be due to the branching of the chain, or to some other factor, cannot be stated without further experimentation.

From the results of this investigation and those of previous workers, the migratory tendencies of various aromatic radicals may be arranged in the following series: (the migratory tendency of the phenyl radical has been chosen as unity) p-anisyl, about 40; a-naphthyl, about 18; *p*-tolyl, 12–15; *p*-biphenyl,[2] 12.5; p-isopropylphenyl, 9; *p*-ethylphenyl, 5; *p*-fluorophenyl,[7] 1.86; *p*-iodophenyl,[7] 1; phenyl, 1; *p*-bromophenyl,[1] 0.75; *p*-chlorophenyl,[1] 0.66; m-tolyl, 0.6; m-anisyl, 0.2; o- and *m*-bromophenyl, o- and *m*-chlorophenyl[7]; o-tolyl, o-anisyl, very small. It is known also that the β-naphthyl group has a much larger migratory tendency than the phenyl group,[5] but just how much larger has not been determined.

Summary

1. Ten aromatic pinacols have been subjected to rearrangement, and the relative effect of various substituents in the phenyl group has been noted.

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[9] Tiffeneau and Orekhoff, *Bull. soc. chim.*, **37, 430** (1925).

2. The various groups have been arranged in order of their migratory tendencies. Definite values have been assigned when possible.

3. *m*-Methoxy cyanobenzene, m-methoxybenzamide, benzoyl-4,4'-di-isopropyltriphenylmethane, and 4,4'-di-isopropyltriphenylmethane have been described, in addition to the ten pinacols, none of which has previously been reported in the literature.

URBANA, ILLINOIS

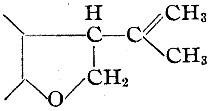
[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. VIII. ISOMERIC HYDROXY ACIDS AND THEIR RELATION TO DEHYDROROTENONE

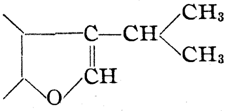
BY F. B. LAFORGE AND L. E. SMITH

RECEIVED MAY 14, 1930 PUBLISHED SEPTEMBER 5, 1930

Rotenone is converted by a number of oxidizing agents into dehydrorotenone, with the loss of two hydrogen atoms. In a recent article, Butenandt has shown that a double bond is formed in this process.[1] Although this new double bond cannot be reduced by catalytic hydrogenation, its presence in dehydrorotenone can be demonstrated by the reaction of Diels,[2] which involves a condensation of a conjugated system with maleic anhydride. It has also been demonstrated that the optically active tubaic acid obtained by cleavage of rotenone with alcoholic potassium hydroxide is converted into inactive rotenic acid under the same conditions by which rotenone is converted into isorotenone and that isorotenone yields rotenic acid by cleavage with alcoholic potassium hydroxide.[1,3] It follows from these facts with a fair degree of certainty that the isomerism between rotenone and isorotenone is due to the same cause as the isomerism between tubaic and rotenic acids. The change involved may be illustrated by the tentative formulas I and II. In these formulas the positions of attachment of the side chain, as well as that of the hydroxyl and carboxyl groups not shown in the figures are as yet undetermined.[4]



I. Tubaic acid



II. Rotenic acid

Since an asymmetric center disappears in this process and since isorotenone is optically active, Butenandt infers that this compound still contains one or more asymmetric carbon atoms in the other half of the molecule, about which little was known to him at the time.

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[1] Butenandt and Hildebrandt, Ann., 477, 245 (1929).

[2] Diels and Adler, *ibid.*, 460, 102 (1928).

[3] Takei, *Ber.*, 63, 508 (1930); Haller and LaForge, THIS JOURNAL, 52, 2480 (1930).

[4] Haller and LaForge, *ibid.*, 52, 3207 (1930).

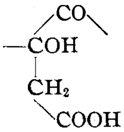
Cehydroisorotenone described by Butenandt and by us[6] is optically inactive whether prepared from isorotenone by the action of iodine and potassium acetate or by the conversion of dehydrorotenone into its isomer by sulfuric acid. It follows from this, as Butenandt has pointed out, that an asymmetric center has disappeared in the formation of the dehydro derivatives.

This theory seemed to be in agreement with the principal facts observed by us regarding the mechanism of the formation of the dehydro compound~.~

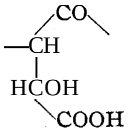
We have described an intermediary product, rotenolone, isolated from the reaction mixture obtained when iodine and potassium acetate react on rotenone.[5] Rotenolone is an hydroxy rotenone and is easily converted into dehydrorotenone by elimination of water.

Dehydrorotenone is converted into a dihydroxy monobasic acid by the action of alcoholic potassium hydroxide, a reaction which is assumed to involve the addition of one molecule of water to the new double bond characteristic of the dehydro derivatives and another molecule of water to the lactone group ta form the acid radical.

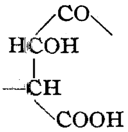
The resulting acid most likely contains one of the following groupings



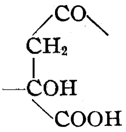
III



IV



V



VI

Dehydrorotenone is converted by catalytic hydrogenation into dehydrodihydrorotenonic acid, which in turn is converted into an hydroxy acid which also contains the same grouping as the acid just referred to.[6] Both give derric acid on oxidation.

In a previous article we have shown that this oxidation product, which represents the part of the rotenone molecule containing the methoxyl groups, in all probability is of the nature of a dimethoxy phenyl malic acid and would therefore contain one of the groupings given above.[7] Rut since the carbonyl group in these groupings becomes a carboxyl group in derric acid, the possibilities are then limited to two combinations, since III and VI and IV and V become identical.

We have just pointed out the fact that the dehydro derivatives are formed from hydroxy derivatives of the rotenolone type by elimination

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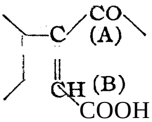
[5] LaForge and Smith, THIS JOURNAL, 52, 1094 (1930).

[6] We have designated acids of this type as dehydro hydroxy acids in previous articles because they were obtained from dehydro compounds, but since it is now fairly certain that they correspond to rotenonic acid, the prefix "dehydro" has been discontinued.

[7] LaForge and Smith, THIS JOURNAL, 52, 2878 (1930).

of water. This reaction is easily brought about by boiling the hydroxyl derivative or the corresponding acetyl compounds with alcoholic sulfuric acid. This reaction does not take place in the case of denic acid or either of the hydroxy acids from which it is obtained. For this reason the position of the hydroxyl group in rotenolone cannot be the same as in these acids.

If we assume that the hydroxy acids are formed by the addition of water to dehydrodihydrorotenonic acid of possible formula indicated, it will be apparent that there are a number of possibilities, depending on whether the hydroxyl is added at position A or B. If it is added at A, one asymmetric carbon atom arises, if at B, two are formed, and the number of possible compounds is multiplied by two, because the part of the molecule not involved in these changes already contains an asymmetric carbon atom. Because of the fact that derric acid and the two hydroxy acids which had' been prepared did not revert to dehydro compounds when treated with alcoholic sulfuric acid, we were inclined to another theory regarding the nature of the dehydro compounds.[7]



We have, however, lately prepared two dihydrohydroxyrotenonic acids, isomeric with the one obtained by the action of alcoholic potassium hydroxide on dehydrodihydrorotenonic acid. These new acids are readily dehydrated by alcoholic sulfuric acid and give dehydrodihydrorotenonic acid. Because of these new facts it is now possible to bring our views into harmony with the theory of Butenandt. It is not possible to assign the position of the hydroxyl in any of the acids concerned but for convenience we will designate those compounds which are easily dehydrated as belonging to the alpha, and those which cannot be dehydrated to the beta series.

One of the two new alpha acids was prepared in two ways: by reducing rotenolone with hydrogen and platinum catalyst which yielded dihydrorotenolonic acid together with dihydrorotenolone, or by catalytic reduction of acetylrotenolone to dihydro-acetylrotenolone and dihydro-acetylrotenolonic acid. The latter is easily saponified to the hydroxy acid.

The second acid was obtained by oxidation of rotenonic acid with hydrogen peroxide in alkaline solution. The products obtained were an hydroxyrotenonic acid of formula $C_{23}H_{24}O_7$ together with some of the corresponding dehydro acid of formula $C_{23}H_{22}O_6$. The hydroxy acid is easily reduced by catalytic hydrogenation to the dihydro acid. Both of these isomeric dihydrohydroxy acids readily give dehydrodihydrorotenonic acid when treated with alcoholic sulfuric acid. From the acid ($C_{23}H_{24}O_7$) obtained directly from rotenonic acid, dehydrorotenonic acid was obtained for the first time, for it had not been possible to reduce the lactone ring in dehydrorotenone without reduction of the double bond so that dehydrodihydrorotenonic acid was always obtained. Dehydrorotenonic acid is readily hydrogenated to the dihydro derivative.

We have also made some alkaline peroxide oxidations on two other rotenone derivatives with rather unexpected results. The acid of formula $C_{23}H_{22}O_8$ (dihydrodehydrohydroxyrotenononic acid), described by us in a previous communication, obtained by the action of strong alcoholic potassium hydroxide on dihydrorotenonone yielded no derric acid or corresponding methoxyl-containing compound but dihydrotubaic acid as the only crystalline reaction product.

This fact is an additional proof that the reaction leading to the compounds of the rotenonone type do not take place in the part of the rotenone represented by tubaic acid, but in the other half of the molecule.

We have expressed the view in a previous article[5] that dihydrodehydrohydroxyrotenononic acid was formed by the opening of a lactone ring and not as Butenandt believed by a benzilic acid rearrangement. We have been able to prove our theory to be correct by the fact that the acid easily reverts to dihydrodehydrorotenonone by boiling in acetic acid solution.

Dehydrodihydrorotenonic acid did not yield derric acid on oxidation with hydrogen peroxide but gave the acid of formula[7] $C_{11}H_{12}O_7$ which we obtained from derric acid by permanganate oxidation.

We have made numerous attempts to separate derric acid into its optically active components. Its brucine salt crystallizes well, but after four recrystallizations the derric acid from it was still inactive. No other suitable alkaloid salts were obtained.

β-Dihydrohydroxyrotenonic Acid.—One and eight-tenths grams of dehydrodihydrorotenonic acid5 was refluxed for four and one-half hours with 18 cc. of 15% potassium hydroxide, 54 cc. of ethyl alcohol and 3.6 g. of zinc powder. After removal of the zinc by filtration, the solution was acidified with dilute hydrochloric acid, and water was added until it became turbid. The white crystalline compound so obtained was recrystallized from dilute ethyl alcohol. The yield was 1.5 g. The compound begins to darken at 192° and melts at 198°.

Anal. Subs., 0.0727: CO_2, 0.1779; H_2O, 0.0425. Calcd. for $C_{23}H_{26}O_7$: C, 66.67; H, 6.27. Found: C, 66.73; H, 6.49.

Oxidation of p-Dihydrohydroxyrotenonic Acid to Derric Acid.—One and a half grams of the acid was dissolved in 18 cc. of 5% potassium hydroxide and to the hot solution 5 cc. of 30% hydrogen peroxide was added in small portions. A small amount of tarry matter which formed was removed mechanically. After being boiled to remove the excess of hydrogen peroxide the solution was cooled and acidified with dilute hydrochloric acid and extracted with ether. The ether solution dried over sodium sulfate gave on evaporation derric acid in a yield of 0.25 g. It was recrystallized from ethyl acetate–n-butyl ether, and melted at 170°. Mixed with derric acid it melted at 170".

Acetyl a-Dihydrorotenolonic Acid (Acetyl a-Dihydrohydroxyrotenonic Acid).—Three grams of acetylrotenolone was reduced in ethyl acetate solution with 0.2 g. of platinum oxide catalyst. In about thirty minutes 252 cc. of hydrogen had been absorbed, and the reaction stopped. The theoretical quantity of hydrogen corresponding to two molecules is calculated as 295 cc. The solution was diluted with ether and extracted with ice cold 2% aqueous potassium hydroxide solution The material insoluble in alkali was isolated by evaporation of the dried ether–ethyl acetate solution. It was recrystallized from methyl alcohol and melted at 189°. It was identical with acetyldihydrorotenolone obtained from dihydrorotenone by the iodine potassium acetate method. The yield was 0.5 g. The aqueous alkaline extract yielded 2 g. of acetyldihydrorotenolonic acid melting between 210 and 214° with decomposition.

Anal. Subs., 0.0687: CO_2, 0.1668; H_2O, 0 0390. Calcd. for $C_{25}H_{28}O_8$: C, 65.79; H, 6.14. Found: C, 66 21; H, 6 31.

Dihydrorotenolonic Acid **(a-Dihydrohydroxyrotenonic** Acid).—This acid may be obtained either by saponification of acetyldihydrorotenolonic acid or by direct hydrogenation of rotenolone, and separation of the reaction mixture into neutral and acid fractions. By the last-mentioned method the yield of acid is small and hence the first procedure is to be preferred. Two grams of acetyldihydrorotenolonic acid was boiled for two hours with slightly more than the calculated quantity of half normal potassium hydroxide. The solution was acidified and the precipitated acid dissolved in ether. After drying and removal of the ether, a sirup was obtained which crystallized completely after seeding with crystals obtained by hydrogenation of rotenolone. The compound is extremely soluble in all reagents except water and petroleum ether. We have not succeeded in recrystallizing it.

Acetyldihydrorotenolonic acid readily gives dehydrodihydrorotenonic acid when boiled for about an hour with 10 parts of 10% alcoholic sulfuric acid and an equal volume of hot water is added to it. Dehydrodihydrorotenonic acid was identified by its melting point, mixed melting point and an optical examination of the crystals. The crude dihydrorotenolonic acid, treated in the same manner, gives the same compound.

Oxidation of Rotenonic Acid with Hydrogen Peroxide.—Two grams of rotenonic[8] acid is dissolved in 25 cc. of 5% potassium hydroxide and to the warm solution 30% hydrogen peroxide is added in small portions until a precipitate is produced. About 8 cc. is usually required. The reaction mixture is boiled for a few minutes and then cooled and saturated with carbon dioxide. A heavy precipitate is formed which is extracted with ether and the solution dried over sodium sulfate.[9] The ether residue contains two compounds. It is dissolved in methyl alcohol from which a small quantity of a yellow compound crystallized on cooling. It melted at 225°. The analysis agrees for dehydrorotenonic acid.

Anal. Subs., 0.0608: CO_2, 0.1551; H_2O, 0.0308. Calcd. for $C_{23}H_{22}O_6$: C, 70.05; H, 5.59. Found: C, 69.57; H, 5.61.

When the methyl alcoholic mother liquor is diluted with water the second crystalline compound is obtained which is recrystallized from dilute methyl alcohol. It melts at 137°, and the yield is 0.25 g. The analysis shows it to be an hydroxyrotenonic acid. The compound was dried to constant weight at 110° for analysis.

Anal. Subs., 0.0681, 0.0741: CO_2, 0.1671, 0.1817; H_2O, 0.0367, 0.0394. Subs., 0.0187: AgI, 0.0215. Calcd. for $C_{23}H_{24}O_7$: C, 66.99; H, 5.82; 2OCH_3, 15.04. Found: C, 66.9, 66.87; H, 5.99, 5.90; OCH_3, 15.17. Subs., 0.0146: 0.375 cc. of $N/10$ KOH; mol. wt. calcd. 412; found, 390.

Isomeric **a-Dihydrohydroxyrotenonic** Acid.—One-half gram of α-hydroxyrotenonic acid was reduced in ethyl acetate solution with 0.1 g. of platinum catalyst. The theoretical volume of hydrogen for 1 molecule, 27 cc., was absorbed in a few minutes. The

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[8] LaForge and Smith, THIS JOURNAL, 51, 2578 (1929).

[9] Most acids of the type of rotenolonic acid are insoluble in carbonates and are precipitated from alkaline solution by carbon dioxide.

solution was decanted from the platinum, evaporated to dryness and the substance recrystallized from dilute ethyl alcohol. The compound sinters somewhat, probably due to water or alcohol of crystallization, and melts at 132°. For analysis it was dried to constant weight at *110°*.

Anal. Subs., *0.0608:* CO_2, *0.1474;* H_2O, *0.0342.* Calcd. for $C_{23}H_{26}O_7$: C, *66.66;* H, 6.28. Found: C, 66.11; H, 6.25.

Dehydrorotenonic Acid.—One gram of the hydroxyrotenonic acid was boiled for one and one-half hours with *10* cc. of 10% alcoholic sulfuric acid. When *3* cc. of water was slowly added to the boiling solution, a small quantity of a compound crystallized out at once. The solution was refluxed for fifteen minutes, cooled and the precipitate was filtered off and recrystallized from benzene. It melts at 275°. The yield was *0.13* g.

This compound is stable to alkali. Further study is being made on this substance. The alcoholic mother liquors were diluted with water, and a yellow crystalline compound was obtained which was recrystallized from methyl alcohol. It melted at 225–227°. When mixed with dehydrorotenonic acid obtained directly by the oxidation of rotenonic acid with hydrogen peroxide, the melting point showed no depression.

Dehydrodiiydrorotenonic Acid from Dehydrorotenonic Acid.—Dehydrorotenonic acid was reduced in acetone solution with hydrogen with platinum catalyst in the usual manner. The theoretical amount of hydrogen for the *0.35* g. used, *20* cc., was absorbed in a few minutes. The solution was evaporated to dryness and the compound recrystallized from dilute ethyl alcohol. It melted at 221°. Mixed with dehydrodihydrorotenonic acid it melted at *221°*. The two substances were compared optically by George L. Keenan of the Food, Drug and Insecticide Administration of the Department of Agriculture, and found to be identical.

"In ordinary light this material is of a sulfur-yellow color and consists of very fine needles. In parallel polarized light, crossed nicols, the extinction is straight and the sign of elongation negative. Nothing significant is shown in convergent polarized light with crossed nicols. The refractive indices are: $-n_\alpha = 1.470$ (commonly shown lengthwise); $n_\beta = 1.690$; $n_\gamma = 1.737$ (commonly shown crosswise); all ±0.003."

Oxidation of Dihydrodihydroxyrotenononic Acid[6] with Hydrogen Peroxide.—Two grams of the acid was dissolved in *30* cc. of 5% potassium hydroxide, and 8 cc. of 30% hydrogen peroxide was added in small portions. After boiling for a few minutes the solution was cooled and made acid with dilute hydrochloric acid. A light yellow material crystallized out, which was recrystallized from dilute methyl alcohol. It melted at *167"*. The yield was *0.3* g. The compound contains no methoxyl group. When mixed with dihydrotubaic acid of melting point 167°, the melting point showed no depression.

Oxidation of Dehydrodihydrorotenonic Acid with Hydrogen Peroxide.—One and three-tenths grams of acid was dissolved in *17* cc. of 5% potassium hydroxide solution, and *5* cc. of 30% hydrogen peroxide was added in small portions. After boiling for a few minutes the solution was filtered from a small precipitate and cooled. On acidifying with dilute hydrochloric acid, a crystalline material was obtained which was recrystallized from *95%* ethyl alcohol. It melted at 262° with decomposition. The yield was *0.2* g.

Anal. Subs., *0.0658:* CO_2, *0.1247;* H_2O, *0.0272.* Calcd. for $C_{11}H_{12}O_7$: C, *51.56; H, 4.68.* Found: C, *51.68;* H, *4.59.* Subs., *0.0187: 1.55* cc. of $N/10$ KOH; mol. wt. calcd., *256;* found, *241.*

The compound is identical with the acid obtained by the oxidation of derric acid.

Dihydrorotenonone from Dehydrodihydrorotenononic Acid.—When dehydrodihydrorotenononic acid is boiled with glacial acetic acid for a few minutes the solution becomes very dark and on cooling, a yellow compound crystallizes out, melting at *288"*.

The yield is about 25% of the theoretical. Mr. Keenan has found the compound to be optically identical with dihydrorotenonone.

Anal. Subs., 0.0647: CO_2, 0.1605; H_2O, 0.0286. Calcd. for $C_{23}H_{20}O_7$: C, 67.61; H, 4.93. Found: C, 67.66; H, 4.89.

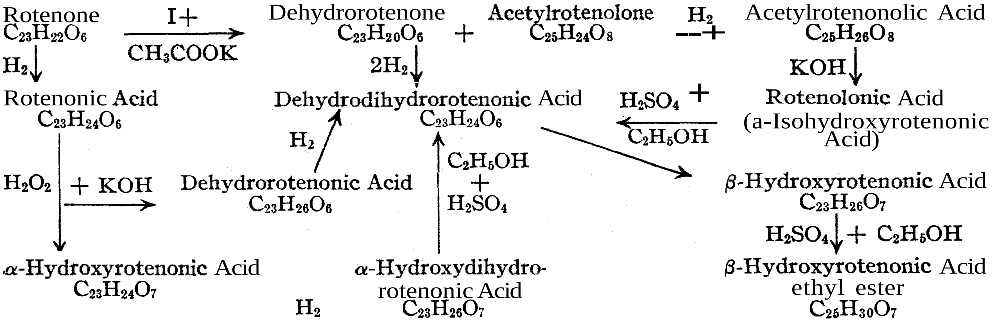
Summary

Dehydrodihydrorotenonic acid is formed by catalytic reduction of dehydrorotenone. It is also produced by dehydration of α-hydroxyrotenonic acids by alcoholic sulfuric acid. Two isomeric alpha acids were prepared.

Dehydrodihydrorotenone adds water when boiled with alcoholic potassium hydroxide to form β-hydroxyrotenonic acid which cannot be dehydrated but yields an ester when treated with alcoholic sulfuric acid. β-Hydroxyrotenonic acid yields derric acid on peroxide oxidation.

Dehydrodihydrorotenonic acid yielded no derric acid but its oxidation product of formula $C_{11}H_{12}O_7$. By the same treatment dihydrodehydrohydroxyrotenononic acid gave dihydrotubaic acid.

Attempts to separate derric acid into optical isomers were unsuccessful. The reactions involved are illustrated in the table.



WASHINGTON, D. C.

[CONTRIBUTION FROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS WELLCOME AND COMPANY]

1,2-DIHYDROPAPAVERINE AND MODIFIED SYNTHESES OF PAPAVERINE AND PAPAVERALDINE (XANTHALINE)

BY JOHANNES S. BUCK

RECEIVED MAY 17, 1930 PUBLISHED SEPTEMBER 5, 1930

A number of investigations have been carried out on the reduction products of papaverine, but 1,2-dihydropapaverine or 6,7,3′,4′-tetramethoxy-1,2-dihydroprotopapaverine[1] (IV) has not been previously isolated. Pyman[2] described a compound of the same empirical formula, which he supposed to have the structure of the 1,2-derivative. Later[3] he modified this view on the basis of exhaustive methylation experiments, and assigned to it the structure (VIII), naming it Pavine.

The writer has obtained 1.2-dihydropapaverine by a rigid method and has established the structure. Homoveratroyl-w-amino-acetoveratrone (I), prepared from homoveratroyl chloride and o-amino-acetoveratrone, was cyclized by means of phosphorus oxychloride, yielding 6,7,3′,4′-tetramethoxy-4-keto-3,4-dihydroprotopapaverine (II). This compound on reduction gave 6,7,3′,4′-tetramethoxy-4-hydroxy-1,2,3,4-tetrahydroprotopapaverine (111), which on appropriate treatment lost the elements of water, 1,2-dihydropapaverine being formed (IV). The structure was established by its smooth reduction (catalytic) to the known tetrahydropapaverine[2] (VII), by its dehydrogenation to papaverine (IX) and by its oxidation to 6,7,3′,4′-tetramethoxy-9-keto-1,2-dihydroprotopapaverine (V), which in turn is readily converted into papaveraldine (VI) or 6,7,3′,4′-tetramethoxy-9-keto-protopapaverine. Papaveraldine is identical with the naturally-occurring alkaloid xanthaline.[4]

The dehydration of (III) to 1,2-dihydropapaverine was carried out by means of phosphorus pentachloride in cold chloroform solution. When heating with phosphorus pentoxide or oxychloride in toluene was employed, only the oxidized product (V) was isolated. The same product was also formed by air oxidation of solutions of 1,2-dihydropapaverine exactly as with 6,7,3′,4′-tetramethoxy-3,4-dihydroprotopapaverine.[5] The parallel is even closer, as 1,2-dihydropapaverine behaves exactly like the latter compound (3,4-dihydropapaverine) when heated with methyl alcoholic potash, both giving papaveraldine (VI).

It was hoped to obtain interesting derivatives from the compounds (II)

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[1] The nomenclature of Buck, Perkin and Stevens, *J. Chem. Soc.*, 127, 1462 (1925). is used except where well-established names exist.

[2] Pyman, *zbzd.*, 95, 1610 (1909).

[3] Pyman and Reynolds, *ibid.*, 97, 1320 (1910); Pyman, *zbzd.*, 107, 176 (1915).

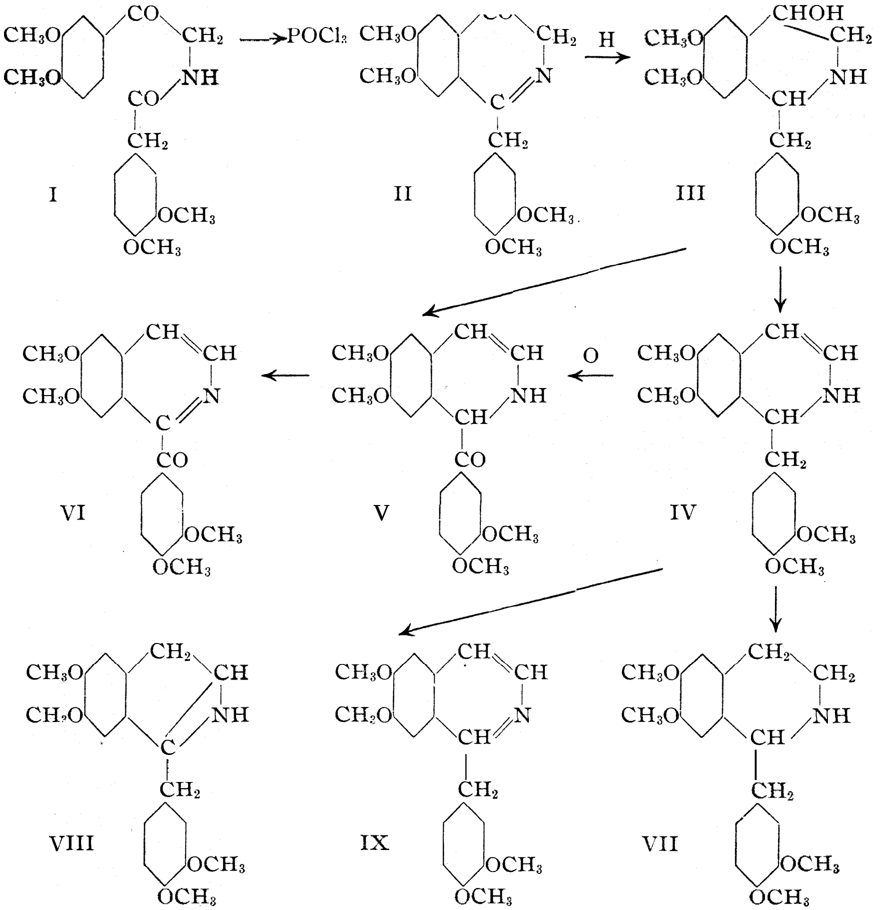
[4] Dobson and Perkin, *ibid.*, 99, 135 (1911).

[5] Buck, Haworth and Perkin, *ibid.*, 125, 2176 (1924).

and (III) but they proved to be disappointingly inert. No derivatives of the carbonyl or hydroxyl groups were isolated, and the basic properties are so suppressed that the bases form no well-defined salts. Indeed (III) may be recrystallized unchanged from fairly strong hydrochloric acid.

1,2-Dihydropapaverine is conspicuous by its ready oxidizability in air, when in solution, and by its very insoluble perchlorate. But for this salt it is doubtful whether 1,2-dihydropapaverine could have been isolated in the pure state.

It will be seen that the isolation of papaverine and papaveraldine (xanthaline) in the above series of reactions constitutes new syntheses of these substances.



Experimental

Homoveratroyl-ω-amino-acetoveratrone (I) was prepared from homoveratroyl chloride and ω-amino-acetoveratrone and was found to be identical with the product of

Pictet and Gams.[6] In preparing homoveratric acid[7] it is advantageous to carry out the oxidation of dimethoxyphenylpyruvic acid with 10% or stronger hydrogen peroxide in the presence of ice, and to recrystallize the acid from benzene.

6,7,3′,4′-Tetramethoxy-4-keto-3,4-dihydroprotopapaverine (II).—Twenty grams of homoveratroyl-w-amino-acetoveratrone, 40 cc. of phosphorus oxychloride and 100 cc. of toluene were boiled for forty-five minutes, cooled and petroleum ether added until no more oil separated. The supernatant liquor was decanted, the oil dissolved in alcohol and sodium hydroxide solution added until the mixture was strongly alkaline. The product separated as an oil and soon solidified; yield almost theoretical. Recrystallized from alcohol the compound forms a white felted mass of slender needles, slightly soluble in cold alcohol and moderately soluble in hot. It is insoluble in water, but readily soluble in cold benzene; m. p. 116–117° (uncorr.). The solution in hydrochloric acid is pale yellow and the solution in chloroform has a marked bluish fluorescence.

With cold concentrated sulfuric acid the solid turns bright blue and gives a blue solution which becomes intensely violet on heating. A crystal of potassium nitrate added to the cold solution gives a deep claret color, changing to crimson. Luchini's reagent gives an orange-brown color, changing to greenish-black, Wenzell's reagent. transient violet, becoming golden: Erdmann's reagent, intense red; Mandelin's reagent, golden brown, greenish on heating: Fröhde's reagent, violet, blue on heating.

It was difficult to obtain concordant analyses on this compound, micro-analyses being usually high and macro-analyses usually low.

Anal. Calcd. for $C_{20}H_{21}O_5N$: C, 67.54; H, 5.67; N, 3.94; mol. wt., 355. Found: C, 67.45; H, 5.99; N, 3.84; mol. wt., 335, 343.

Methiodide.—This was prepared by heating with benzene and methyl iodide in a sealed tube at 100° for two hours. It forms faintly yellow thin square plates, m. p. 202° (uncorr.) with frothing.

Anal. Calcd. for $C_{21}H_{24}O_5NI$: C, 50.7; H, 4.8. Found: C, 50.5; H, 4.8.

6,7,3,′4′-Tetramethoxy-4-hydroxy-1,2,3,4-tetrahydroprotopapaverine (III).—It was not found possible to reduce the compound (II) successfully with the usual reagents, such as zinc and sulfuric acid, etc Ultimately a very active catalyst (platinic chloride in hydrochloric acid with the addition of platinum oxide and Skita catalyst) was prepared. This readily caused the absorption of four atoms of hydrogen (acetic acid with hydrochloric acid as solvent). No stage corresponding to two atoms of hydrogen was isolated. After the catalyst had flocculated, the solution was evaporated under reduced pressure, the residue dissolved in methyl alcohol and treated with ammonia. The product crystallizes out on standing. Recrystallized from alcohol, the compound forms white, bulky aggregates of crystals (thin rectangular plates) melting at 123° (uncorr.). It is slightly soluble in hot water, readily soluble in hot alcohol and moderately soluble in hot toluene.

With cold concentrated sulfuric acid the compound gives a colorless solution, becoming pale amethyst on warming. Addition of a crystal of potassium nitrate to the cold acid solution produces an orange-brown color. Luchini's reagent gives a pale gold color; Wenzell's reagent, violet changing to gold; Erdmann's reagent, light golden; Mandelin's reagent, greenish-gold; Frohde's reagent, green, changing to deep brown.

Anal. Calcd. for $C_{20}H_{25}O_5N$: C, 66.85; H, 6.96. Found: C, 66.72; H, 7.21.

1,2-Dihydropapaverine (IV).—One gram of compound (III) dissolved in 10 cc. of chloroform was treated with 3 g. of phosphorus pentachloride and allowed to stand for forty-eight hours in the cold. The yellow magma which formed was added to crushed ice,

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[6] Pictet and Gams, *Ber.*, 42, 2943 (1909).

[7] Haworth, Perkin and Rankin, J. Chem. *Soc.*, 125, 1693 (1924).

the chloroform layer separated, washed with water and sodium bicarbonate solution and evaporated under reduced pressure. The residual gum was taken up in acetic acid and 20% perchloric acid added. The sparingly soluble perchlorate was filtered off, washed, dried, suspended in benzene and a stream of dry ammonia passed in. After filtration and the addition of petroleum ether, a crop of crystals separated on standing in a refrigerator and was filtered off. The liquor slowly deposits the oxidized compound (V) (below). For this reason, any prolonged operations should be carried out in an atmosphere of inert gas. For analysis, the compound was recrystallized several times from dilute methyl alcohol, after it had been warmed with methyl alcoholic potash to remove impurities. 1,2-Dihydropapaverine forms a bulky white mass of crystals (narrow hexagonal plates) melting at 97–98" (uncorr.). It is easily oxidized in solution by air, or by strong hydrogen peroxide in acetone solution, to the compound (V). It is readily soluble in the usual solvents, sparingly soluble in petroleum ether and practically insoluble in water.

With cold concentrated sulfuric acid it gives a yellow-brown solution which becomes intensely bluish-violet on heating. A crystal of potassium nitrate added to the cold acid solution gives an intense golden-brown color. Boiling acetic anhydride slowly develops a light emerald-green color (see compound V). Luchini's reagent gives a deep red color; Wenzell's reagent, deep violet; Erdmann's reagent, orange-red; Mandelin's reagent, blood-red, golden on heating; Frohde's reagent, yellow-green, becoming deep green, then violet on heating.

Anal. Calcd. for $C_{20}H_{23}O_4N$: C, 70.38; H, 6.74. Found: C, 69.98; H, 6.99.

On catalytic reduction in hydrochloric–acetic acid solution, tetrahydropapaverine is produced. It was isolated and identified by means of the characteristic hydriodide, which was compared with an authentic specimen prepared by Pyman's method. A mixed melting point determination showed no depression.

The dehydrogenation of 1,2-dihydropapaverine went very smoothly when 0.4 g. was heated with 0.2 g. of palladium black[8] in an inert atmosphere for thirty minutes at 170–180°. The melt was extracted with 10% hydrochloric acid and the papaverine precipitated as iodide by the addition of potassium iodide. The iodide was recrystallized from alcohol and identified (properties and mixed melting point determination) by comparison with an authentic specimen, and was then converted into the base and similarly identified as papaverine

1,2-Dihydropapaverine is very similar to 3,4-dihydropapaverine[5,6] and is best distinguished by means of its oxidation product (V), which shows considerable differences from that derived from the 3,4-compound.

Perchlorate.—This was prepared from the purified base and forms a sphaerocrystalline white powder, melting with blackening at 238° (uncorr.) after sintering. It is very sparingly soluble except in strongly acid solutions.

Anal. Calcd. for $C_{20}H_{23}O_4N \cdot HClO_4$: C, 54.36; H, 5.44. Found: C, 54.31; H, 5.74.

Picrate.—Prepared from the purified base, the picrate forms a lemon-yellow sphaerocrystalline powder, melting at 151° (uncorr.).

Anal. Calcd. for $C_{20}H_{23}O_4N \cdot C_6H_3N_3O_7$: C, 54.74; H, 4.56. Found: C, 54.39; H, 4.72.

6,7,3,'4'-Tetramethoxy-9-keto-1,2-dihydroprotopapaverine.—As already mentioned, this compound is produced by air-oxidation of 1,2-dihydropapaverine or by oxidation by strong hydrogen peroxide in acetone solution. When phosphorus pentoxide or oxychloride is used to remove water from (111), this compound is usually obtained. It

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[8] Cf. Spath and Polgar, *Monatsh.*, 51,190 (1929).

forms a compact mass of thick, irregular prisms from alcohol, melting at 187° (uncorr.). It is moderately soluble in alcohol, soluble in chloroform, somewhat soluble in hot benzene and very sparingly soluble in ether. With cold concentrated sulfuric acid it forms a golden solution, which becomes intensely red on adding a crystal of potassium nitrate. It dissolves in hydrochloric acid with a golden color and in hot acetic anhydride with an intense deep-green color. Luchini's reagent gives a red color; Wenzell's reagent, transient violet; Erdmann's reagent, orange red; Mandelin's reagent, blood red, becoming golden on heating; Frohde's reagent, brownish, blood-red when heated.

Anal. Calcd. for $C_{20}H_{21}O_5N$: C, 67.54; H, 5.67. Found: C, 67.22; H, 5.94.

When warmed on the steam-bath with methyl alcoholic potash, the compound rapidly changes into papaveraldine, identified by comparison and mixed melting point determinations with the authentic compound and with the alkaloid xanthaline.

Summary

1,2-Dihydropapaverine, hitherto unknown, has been synthesized and its structure established. In the course of the work, papaverine and papaveraldine have been obtained by a new series of reactions.

TUCKAHOE, NEW YORK

[CONTRIBUTION FROM BOYCE THOMPSON INSTITUTE FOR PLANT RESEARCH, INC., YONKERS, NEW YORK]

AN IODIMETRIC METHOD FOR DETERMINING OXIDASE ACTIVITY[1]

BY JOHN D. GUTHRIE

RECEIVED MAY 17, 1930 PUBLISHED SEPTEMBER 5, 1930

The usual methods for estimating oxidase activity depend on either the production of a colored substance,[2] or the measurement of the volume of oxygen absorbed.[3] Recently an electrometric method has been suggested.[4] Colorimetric methods are often inapplicable on account of pigments or turbidity in the extracts to be tested. Methods measuring the oxygen uptake require special apparatus. The method to be described here requires no unusual equipment, is easy to use and reasonably accurate. With it as many as sixteen determinations have been made at the same time.

In a previous paper,[5] it was noted that potato juice contains a substance or substances that may be titrated with iodine in acid solution (trichloroacetic acid) and that this titration decreases on exposure to air. Ordinarily five cc. of juice reduces about 0.5 cc. of $N/100$ iodine. However, juice from one lot of potatoes was found to reduce 2.0 cc. of $N/100$ iodine. It was thought that this might be due to a low content of oxidase, the substance responsible for the iodine reaction not being oxidized in the

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[1] Herman Frasch Foundation for Research in Agricultural Chemistry, Paper No. 6.

[2] J. A. Dye, *Proc. Soc. Exptl. Biol. Med.*, 24, 640–642 (1927).

[3] H. H. Bunzel, THIS JOURNAL, 34, 303–316 (1912).

[4] A. E. Stearn and A. A. Day, *J. Biol. Chem.*, 85, 299–306 (1929).

[5] F. E. Denny, L. P. Miller and J. D. Guthrie, *Am. J. Botany*, 17, 483–509 (1930).

process of extraction for this reason. In order to test this point, juice of this lot of potatoes was boiled and filtered. It still reduced 2.0 cc. of $N/100$ iodine. To 50-cc. portions of this boiled, filtered juice, 1 cc. of fresh juice from the same lot of potatoes and also 1 cc. from a lot giving the usual iodine titration were added. On exposing these mixtures to air in a thin layer, the iodine titration of the one containing the juice suspected of being low in oxidase had decreased 0.8 cc. after forty-five minutes, while the titration of the one containing juice of the other lot had decreased 1.4 cc. A water blank decreased 0.2 *cc.*

These results suggested that if a substance could be found that would reduce iodine in acid solution and which would also be oxidized by the air in the presence of potato juice, a convenient method would be available for determining oxidase. Cysteine was first tried. Its oxidation is catalyzed by potato juice, but the reaction proved to be autocatalytic and therefore unsuitable for the purpose. The autocatalytic nature of the oxidation of cysteine has been previously noted.[6]

Szent Gyorgyi[7] has noted the iodine reaction of plant juices and has isolated a substance that reduces iodine in acid solution from the adrenal cortex, orange and cabbage. He finds it to be a hexuronic acid. For this reason glucose that had been warmed with dilute sodium hydroxide was tried, since this product is known to contain a great variety of carbohydrate derivatives and it was thought that some of these might reduce iodine in acid solution. It was found that the iodine titration was quite large. Tests showed that it decreased on exposure to air and that this oxidation was catalyzed by potato juice.

Preliminary Work.—During the first part of the work, the reaction was carried out in liter beakers, 25 cc. of the reacting mixture being exposed in a thin layer in the bottom. At intervals, 5-cc. aliquots were drawn, 10 cc. of 10% trichloro-acetic acid was added and titrated with $N/100$ iodine, using starch as an indicator. The first difficulty encountered was a high blank, but it was found that clearing the substrate with decolorizing charcoal obviated this. It was also found that the conditions for aeration were unsatisfactory, since the rate of oxidation ceased to be directly proportional to the concentration of enzyme when more than 1 cc. of potato juice was used. Carrying out the reaction in aeration tubes corrected this difficulty. This improvement necessitated the use of a foam breaker. Capryl alcohol was tried, but all samples available interfered with the end-point, probably due to some impurity. It also had a slight retarding effect. Amyl alcohol, while not affecting the end-point, was decidedly injurious to the enzyme. Paraffin oil, although not so efficient a foam breaker as the higher alcohols, was finally chosen. In

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[6] M. Dixon and H. E. Tunnicliffe, *Proc.* Roy. *Soc.* (London), **94B,** 266–297 (1923).

[7] Szent Gyorgyi, *Biochem. J., 22,* 1387–1409 (1928).

order to test the effect of foaming, the addition of digitonin was tried. It greatly increased foaming but did not affect the results. As an additional improvement it was found that more accurate results could be obtained by adding a known quantity of iodine, allowing to stand and then titrating the excess with thiosulfate.

Preparation of Substrate.—Dissolve 40 g. of glucose in 400 cc. of N sodium hydroxide, place it in a 500-cc. Florence flask and immerse in a water-bath at 80° for fifteen minutes. Remove and neutralize at once by adding 10 cc. of 85% phosphoric acid. Add 25 g. of decolorizing charcoal (Norit A was used) and allow to stand overnight. Filter and add 25 g. of decolorizing charcoal to the filtrate. Allow to stand for fifteen minutes and filter. Dilute a small portion of the filtrate about one to five and determine the PH value. If it is not close to PH 6.5, adjust to this PH with N sodium hydroxide or N hydrochloric acid. The addition of 2 cc. of either to 100 cc. of the filtrate shifts the acidity about 0.1 *PH*. The iodine value for 25 cc. should be equal to about 60 cc. of *N*/50. Before using, dilute the filtrate with an equal volume of water.

The Method.—Pipet 25-cc. portions of the diluted substrate into Van Slyke–Cullen[8] aeration tubes. Add 2 cc. of the juice or extract containing the enzyme. For each determination run a blank, using 2 cc. of the boiled, filtered juice or extract. Add five drops of paraffin oil to each tube and aerate for one hour. Wash into 300-cc. Erlenmeyer flasks containing 25 cc. of 10% trichloro-acetic acid, adding in all about 50 cc. of water. Add 50 cc. of *N*/50 iodine in *N*/10 potassium iodide and allow to stand for thirty minutes. Titrate with *N*/100 sodium thiosulfate, using 1 cc. of 1% starch paste as an indicator. Titrate the blank first and the determination immediately afterward. The difference between these titrations is a measure of the oxidase activity of the sample.

Accuracy of the Method.—In order to test how nearly results could be duplicated, twelve determinations were made on the same lot of potato juice. The average value was 6.15 cc. with an average error of ±0.15 cc. To see how nearly the substrate could be duplicated, four batches were prepared and used with the same potato juice. The average value was 6.50 cc. with an average error of ±0.2 cc. This was repeated with four other batches of substrate and other potato juice. The average value was 6.8 cc. with an average error of ±0.15 cc.

Choice of PH Value.—Acidity of the reacting medium greatly affects the activity of enzymes. Therefore, a series of determinations was made at various PH values. These were obtained by the addition of N sodium hydroxide or N hydrochloric acid to the substrate. The quinhydrone electrode was used. Some difficulty was experienced, probably due to the interference of reducing substances. On the concentrated substrate values that were too alkaline were obtained. More acid values, which are believed to represent nearly the true PH, were obtained by diluting with about five volumes of water and using a large amount of quinhydrone. This effect is probably brought about by diluting the interfering substances and thereby minimizing their effect. Several experiments were made to determine the effect of the PH value of the substrate. A curve showing one of these, which is typical of the others, is shown in Fig. 1. Between PH 6.0 and PH 7.0 the oxidase activity is not greatly affected. Therefore, PH 6.5 was chosen as the best for carrying out the determinations. Bunzell[9] has investigated the effect of hydrogen-ion concentration on oxidase activity and recommends approximate neutrality for making the determinations. His data, however, are insufficient to show the exact form of the PH–oxidase curve, especially between PH 6.0 and 7.0.

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[8] D. D. Van Slyke and G. E. Cullen, J. *Biol. Chem.*, 19, 211–218 (1914).

[9] H. H. Bunzell, *ibid.*, 28, 315–333 (1916).

Effect of Concentration of Enzyme and **Time** of Aeration.—In order to test the effect of the concentration of enzyme and decide on the time of aeration, experiments were made using one, two, three and four cc. of potato juice and aerating for different periods. In the first experiments which were aerated for two hours the oxidase activity was not linear with the concentration, but curved upward. This tendency was negligible

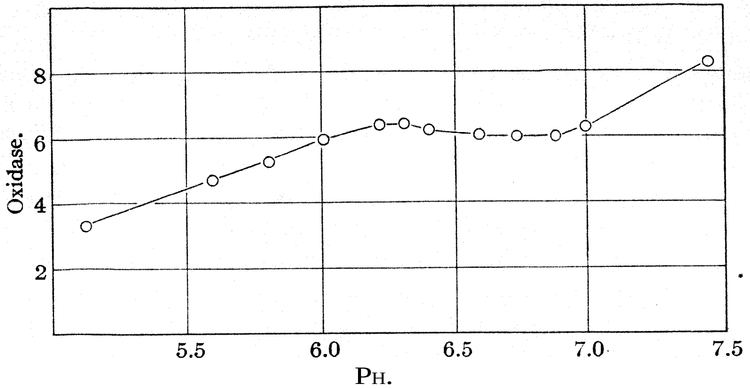
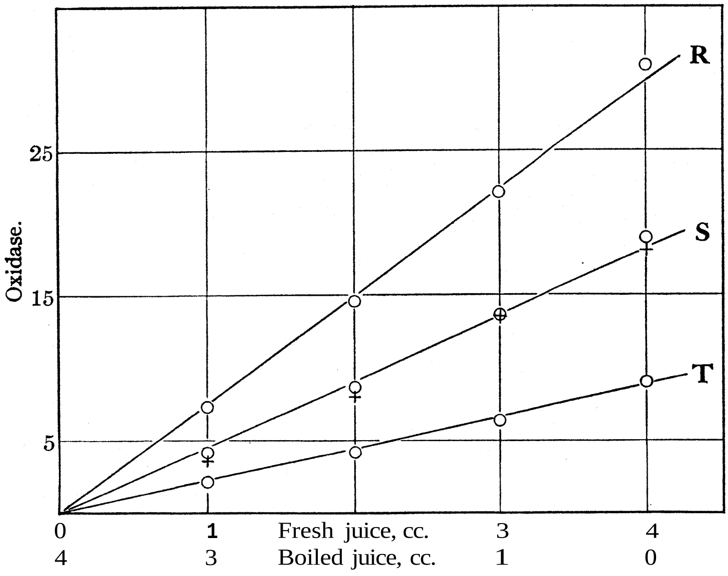


Fig. 1.—Showing the effect of hydrogen-ion concentration on the oxidase activity of potato juice. Aerated for one hour; two cc. of juice used.



R, 120 minutes; S, 60 minutes; T, 30 minutes.

Fig. 2.—Showing the effect of enzyme concentration and time of aeration. Circles determined with usual substrate concentration, crosses with half this concentration.

when the aeration was only for one hour. It was found that the reason for this was the protective action of the juice, the enzyme in the tubes containing the larger amounts of juice being better protected. This protective action is present in the boiled, filtered juice. Therefore, an experiment was made in which the tube with 1 cc. of fresh juice contained also **3** cc. of boiled juice, the tube with 2 cc. of fresh juice, 2 cc. of boiled juice, and so on. Thus each tube contained 4 cc. of juice, but different amounts of enzyme in each. The results are shown in Fig. 2. It will be seen that the oxidase activity is almost linear with the concentration of enzyme even with two hours' aerating. Up to one hour the reaction is linear with time. In the second hour the reaction goes more slowly, showing that some enzyme is being destroyed. Therefore, one hour has been chosen for the time of aeration. Points are also given for the one-hour aeration curve in which half the usual concentration of substrate was used. Very little difference is noted, showing that in this range substrate concentration is not an important factor.

Results with Other Plants.—In order to see if the methods could be used on other materials besides potato juice, several other plant juices were tried. The results are shown in Table I. Qualitative tests were also made with the indophenol reagent.[10] The quantitative results correlate well with the qualitative.

TABLE I

APPLICATION OF METHOD TO VARIOUS PLANTS. TWO CC. OF JUICE USED UNLESS OTHERWISE NOTED

Plant	Iodimetric oxidase		Indophenol oxidase
Onion (bulb)	**0.6**	**0.4**	
Turnip (root)	**0.3**	**0 3**	−
Beet (root)	7.7	**8 3**	++
Beet (leaves)	7 6	**7.7**	++
Carrot (root)	**2.3**	**2** 5	+
Apple (fruit)	**2 6**	**2 2**	++
Tomato (leaves) 0.5 **cc.**	**11.8**		+++++
Tomato (stems) 0.5 **cc.**	**1.3**		++
Tobacco (healthy leaves) 0.5 **cc.**	**4 4**		+++
Tobacco (mosaic leaves) 0.5 **cc.**	**12.8**		+++++

Summary

An iodimetric method is given for the estimation of oxidase activity. Oxidase activity as measured by the method is a linear function of the enzyme concentration. The effect of hydrogen-ion concentration on potato oxidase has been studied. The method is applicable to a variety of plants.

YONKERS, NEW YORK

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[10] **H. M. Vernon,** *J. Physiol.*, **42, 402432 (1911)**

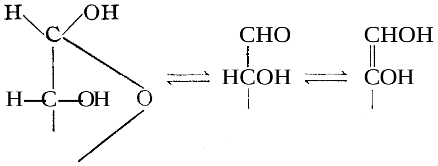
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

ALDEHYDO-I-ARABINOSE TETRA-ACETATE[1]

BY M. L. WOLFROM AND MILDRED R. NEWLIN

RECEIVED MAY 21, 1930 PUBLISHED SEPTEMBER 5, 1930

In continuation of the studies being made in this Laboratory on the open-chain forms of the sugar acetates, we wish to report in this paper the synthesis of the crystalline free aldehyde form of *l*-arabinose tetra-acetate. Although the ring formulas for the monosaccharides meet the requirements imposed by experimental data in most cases, there are nevertheless many reactions which are best explained by the assumption of an open-chain form in equilibrium with the ring or lactal structures. This is particularly true of the reactivity of the sugars in alkaline media. The changes that I-arabinose undergoes in alkaline solutions have been studied by Nef[2] and by Evans and Conaway.[3] These changes are best explained on the basis of enolic equilibria, which then require an intermediate open-chain formula, as follows



This paper presents evidence that the free aldehyde form of *l*-arabinose is capable of stable existence in the form of its crystalline acetate, $CH_2OAc-(CHOAc)_3-CHO$.

The methods used were similar to those reported in the case of glucose[4] and of galactose.[5] Arabinose ethyl mercaptal was acetylated and the thioethoxy groups replaced by an oxygen atom through reaction with mercuric chloride[6] and water under controlled conditions. The modifications introduced to obtain the arabinose compound consisted in the use of less water in the reaction and a slightly different method of isolation.

The free aldehyde form of *l*-arabinose acetate or aldehydo[5]-*l*-arabinose tetra-acetate crystallizes in prismatic needles and has widely differing constants from the two known lactal acetates of this sugar. Chavanne[7] first obtained crystals of the a-form of arabinose tetra-acetate, but in too

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[1] Constructed from a thesis presented by Mildred R. Newlin in candidacy for the degree of Master of Science at The Ohio State University.

[2] J. U. Nef, Ann., 357,214 (1907); **376,** 1 (1910); 403,204 (1914).

[3] R. F. Conaway, Ph.D. Dissertation, The Ohio State University, 1929.

[4] M. L. Wolfrom, THIS JOURNAL, 51,2188 (1929).

[5] M. L. Wolfrom, *ibid.,* 52, 2464 (1930).

[6] Cf. P. **A.** Levene and G. M. Meyer, **J.** *Biol. Chem.,* 69,175 (1926); 74,695 (1927).

[7] G. Chavanne, *Compt.* rend.. 134,661 (1902).

small amount to analyze. Hudson and Dale[8] have synthesized and characterized a- and β-*l*-arabinose tetra-acetates. The properties of the three forms are listed in Table I.

TABLE I

PROPERTIES OF THE THREE TETRA-ACETATES OF *l*-ARABINOSE

Form	M. p. °C.	$[\alpha]_D$, Chloroform
α	97	+ 42.5"
β	86	+147.2°
Aldehydo	114	− 65"

The rotation of aldehydo-*l*-arabinose tetra-acetate was stable in acetylene tetrachloride ($[\alpha]_D^{26}$ −58°) solution and in alcohol-free chloroform but underwent a slow change in the dextro direction in methyl alcohol and U. S. P. chloroform. In the former solvent the initial specific rotation was −46°, changing to −29° in five days. That this is due to combination with the alcohol is made probable by the isolation of well-characterized compounds of this type in the case of galactose.[5] The substance readily gave the Schiff aldehyde test and reduced Fehling's solution. A crystalline semicarbazone was formed without loss of an acetyl group. This semicarbazone showed a normal molecular weight by the Rast[9] method. The aldehydo forms of glucose and galactose acetates showed low specific rotations, being −5 and −25° in chloroform, respectively. This was thought to be probably characteristic of the open-chain forms. However, the value −65° obtained for the arabinose acetate, shows that the carbonyl group may produce a relatively high rotation, in spite of the absence of rings.

Further work on the synthesis and reactivity of the free aldehyde forms of sugar acetates is in progress in this Laboratory.

Experimental

***l*-Arabinose-ethylmercaptal Tetra-acetate.**—Three grams of *l*-arabinose ethyl mercaptal[10] (m. p. 124–126°) was dissolved in 12 cc. of dry pyridine at room temperature and the solution cooled in ice water. To this was added, gradually, 24 cc. of acetic anhydride. Some of the solute precipitated, but redissolved after a short time on standing at 0° with occasional shaking. The solution was then allowed to stand overnight at room temperature. At the end of this period it was poured slowly with stirring into 600 cc. of ice and water. A heavy oil separated which crystallized readily. Recrystallization was effected by dissolving the filtered crude material in methyl alcohol at room temperature, adding water and allowing the mixture to crystallize in the ice box. The yield of the pure product was 4.5 g. or 91%.

The substance crystallizes in prisms and after one recrystallization melted at 79–80". After another recrystallization the melting point was the same and the specific rotation in chloroform was −30.8° at 27° (0.4005 g. subs. in 10.06 cc. U. S. P. chlorcform

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[8] C. S. Hudson and J. K. Dale, THIS JOURNAL, 40, 992 (1918).

[9] K. Rast, *Ber.*, 55, 1051 (1922).

[10] E. Fischer, *ibid.*, 27, 673 (1894).

soln., 1.1-dm. tube, LYD = –1.35°). After four recrystallizations the melting point was 79–80° and the specific rotation in the same solvent was –29.9° at 26° (0.4008 g. subs. in 10.06 cc. U. S. P. chloroform soln., 1.1-dm. tube, α_D = –1.31'). The substance is practically insoluble in cold water, slightly soluble hot, somewhat soluble in ethyl alcohol and petroleum ether, and very soluble in ether, acetone and chloroform.

Anal. Subs., 0.2002: 19.01 cc. 0.1 *N* NaOH. Subs., 0.2001: 19.01 cc. 0.1 *N* NaOH. Calcd. for 100 mg. of $C_5H_6O_4(CH_3CO)_4(SC_2H_5)_2$: cc. 0.1 *N* NaOH, 9.43. *Found:* 9.49, 9.50.

Aldehydo-*l*-arabinose Tetra-acetate.—An amount of 25 g. of *l*-arabinose-ethyl mercaptal tetra-acetate (m. p. 79–80') was dissolved in 90 cc. of pure acetone, and 15 cc. of water added. To this was added with mechanical stirring, an excess, 40 to 50 g., of finely powdered alkali-free cadmium carbonate, then a solution of 59 g. of mercuric chloride in 75 cc. of acetone. Stirring was maintained at room temperature for twelve hours, with occasional additions of fresh cadmium carbonate. The mixture was then held for fifteen minutes in a 50° bath, vigorous stirring being maintained. Finally, the solution was refluxed for fifteen minutes. The solution was cooled and filtered, cadmium carbonate being placed in the suction flask before filtering. The filtrate was then concentrated under reduced pressure at 30–35° in the presence of an excess of cadmium carbonate and dried several times by adding fresh acetone and evaporating under reduced pressure. The residue was extracted with warm chloroform and the extract dried *a* short time with sodium sulfate, adding some norite at the same time. After filtration, the solution was evaporated to dryness at room temperature in a vacuum desiccator. The last traces of chloroform were removed by several treatments with petroleum ether. A partially crystalline mass was thus obtained, from which the crystals were isolated by treatment with alcohol-free, dry ether, which dissolved the sirup. The ether solution was filtered and the crystalline residue washed with ether. The amount of this material was 5 g. and an additional crop of 2 g. was obtained from the ethereal filtrate on standing overnight in the ice box.

For purification, the material was dissolved in the minimum amount of warm acetone, and half the volume of anhydrous and alcohol-free ether added. Petroleum ether was then carefully added, crystallization being effected readily. By this procedure 5 g. of the crude material from the ether treatment gave 3.7 g. of product with m. p. 112–114° (corr.) and showing a specific rotation in acetylene tetrachloride soln. of –57.8° at 26° (0.4008 g. subs. in 10.06 cc. acetylene tetrachloride soln., 1.0-dm. tube, α_D = –2.30"). After three recrystallizations the melting point was 113–115° (corr.) and the specific rotation in the same solvent was –58.0° at 26° (0.4002 g. subs. in 10.06 cc. acetylene tetrachloride soln., 1.0-dm. tube, α_D = –2.31°). After five recrystallizations the melting point remained at 113–115" (corr.).

The substance crystallizes in clusters of prismatic needles. It is slightly soluble in cold water and ethyl alcohol, and readily soluble in these solvents when warmed. It is slightly soluble in warm ether and is practically insoluble in petroleum ether. It dissolves readily in methyl alcohol and with extreme ease in chloroform and acetone. The initial specific rotation of the pure substance in U. S. P. chloroform at 31° was –65.2" (0.4014 g. subs. in 10.06 cc. U. S. P. chloroform soln., 1.0-dm. tube, α_D = –2.60°). This value changed slowly in the dextro direction, being –63.3° after thirty minutes. In alcohol-free chloroform solution the specific rotation at 27" of the pure substance was –65.4° (0.4013 g. subs. in 10.06 cc. chloroform soln., 1.0-dm. tube, α_D = –2.61°). Another determination at the same temperature gave the value –65.6" (0.4017 g. subs in 10.06 cc. chloroform soln., 1.0-dm. tube, α_D = –2.62"). The change in these values in twenty-four hours was negligible. The alcohol-free chloroform was prepared from the U. S. P. grade by washing with water, drying overnight with sodium and calcium chloride and redistilling. In methyl alcohol solution an initial specific rotation of −46° was obtained, changing slowly in the dextro direction. This change is tabulated in Table II.

TABLE II

CHANGE IN ROTATION OF ALDEHYDO-*l*-ARABINOSE TETRA-ACETATE IN METHYL ALCOHOL SOLUTION

l = 1.0 dm. λ 6892 Å.

Experiment 1			Experiment 2		
	t = 30°, c = 3.993			t = 30°, c = 3.995	
Time, hrs.	α, degrees	$[\alpha]_D$, degrees	Time, hrs.	α, degrees	$[\alpha]_D$, degrees
0.03	−1.83	−45.8	0.03	−1.87	−46.8
0.25	−1.82	−45.6	0.25	−1.86	−46.6
0.50	−1.81	−45.3	0.50	−1.85	−46.3
0.75	−1.80	−45.1	..	....	....
1	−1.79	−44.8	1	−1.85	−46.3
1.25	−1.79	−44.8	..	....	....
1.50	−1.77	−44.3	..	....	....
1.75	−1.76	−44.1	..	....	....
19	−1.40	−35.1	..	....	....
24	−1.31	−32.8	24	−1.33	−33.3
72	−1.09	−27.3	..	....	....
..	....	....	96	−1.18	−29.5
..	....	....	120	−1.20	−30.0
144	−0.99	−24.8	144	−1.14	−28.5
168	−0.96	−24.0	168	−1.08	−27.0
192	−0.96	−24.0	..	....	....
216	−0.92	−23.0	..	....	....

Anal. Subs., 0.1000: 12.56 cc. 0.1 N NaOH. Subs., 0.1000: 12.76 cc. 0.1 N NaOH. Subs., 0.2196: CO_2, 0.3939; H_2O, 0.1176. Calcd. for $C_5H_6O_5(CH_3CO)_4$: C, 49.04; H, 5.69; cc. 0.1 N NaOH per 100 mg., 12.6. Found: C, 48.92; H, 5.99; cc. 0.1 N NaOH, 12.6, 12.8; S, absent.

Aldehydo-*l*-arabinose-semicarbazone Tetra-acetate.—An amount of 4 g. (1 mole) of aldehydo-*l*-arabinose tetra-acetate (m. p. 113–115°) was dissolved in 40 cc. of warm water and cooled rapidly to room temperature. A mixture of 2 g. (1.3 moles) of semicarbazide hydrochloride and 2.5 g. (2 moles) of potassium acetate was added and the solution shaken vigorously. The crystalline semicarbazone began to separate rapidly after three to four minutes in the form of glittering four-sided plates. After one recrystallization from methyl alcohol the melting point was 184–187° (corr.) and this value was unchanged on a second recrystallization from hot water. The substance is moderately soluble in chloroform and acetone, soluble in warm water and warm alcohol, and is practically insoluble in ether and petroleum ether.

Molecular weight (Rast). 0.0106 g. subs. in 0.1017 g. of camphor depressed the m. p. 10.5°. Mol. wt. calcd. for $C_{14}H_{21}O_9N_3$: 375. Found: 396.

Anal. Subs., 0.2007: N_2, 19.50 (742.2 mm., 20°). Subs., 0.1000: cc. 0.1 N NaOH, 10.8, 10.7. Calcd. for $C_6H_9O_5N_3(CH_3CO)_4$: N, 11.20, cc. 0.1 N NaOH per 100 mg., 10.7. Found: N, 10.96, cc. 0.1 N NaOH, 10.8, 10.7.

Summary

1. A new form of *l*-arabinose tetra-acetate has been synthesized in pure crystalline condition.

2. Evidence is presented that this substance possesses the free aldehyde structure.
3. The crystalline semicarbazone of this aldehyde has been prepared in pure form.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE CHEMISTRY OF DIARYL SULFIDES. III. THE SYNTHESIS OF THIOTHYRONINE[1]

BY GEORGE H. LAW AND TREAT B. JOHNSON

RECEIVED MAY 22, 1930 PUBLISHED SEPTEMBER 5, 1930

In two previous papers from this Laboratory,[2] attention has been directed to the remarkable effect of diaryl-sulfide groupings in organic compounds which have been shown to have therapeutic value as germicides or antiseptics. The outstanding derivative thus far studied is p-hydroxy-diphenyl-sulfide which was found to possess a germicidal activity equivalent to a phenol coefficient of 115. As a result of the discovery of this unexpected increase in germicidal power, and on account of the growing interest in the biochemistry of organic sulfur groupings in general, we have now extended further our researches in this field, and have begun a study of practical methods for synthesizing sulfur-ether-a-amino acid combinations corresponding in structure to the naturally occurring protein acids, phenyl-alanine and tyrosine, and also the sulfur analog of the hormone—*thyroxine.* In this paper we describe methods of synthesizing the two new α-aminoacids—*p*-methyl-*p'*-diphenylsulfide-β-alanine and p-hydroxy-*p'*-diphenylsulfide-β-alanine or *thiothyronine* (desiodo-thyroxine), which are expressed by formulas I and II, respectively. The amino acid II is the sulfur analog of thyronine III already described by Harington,[3] and is the first aromatic sulfur-ether derivative of the amino acid thiotyrosine IV to be described. A method for preparing *thiotyrosine* IV was first described in a paper from the Yale laboratory by Johnson and Brautlecht[4] in 1912, and so far as the authors are aware no attention has been paid to

$CH_3C_6H_4SC_6H_4CH_2CH(NH_2)COOH$
I

$HOC_6H_4SC_6H_4CH_2CH(NH_2)COOH$
II

$HOC_6H_4OC_6H_4CH_2CH(NH_2)COOH$
III

$HSC_6H_4CH_2CH(NH_2)COOH$
IV

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[1] Constructed from a dissertation presented by George Hartland Law in June, 1929, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

[2] Hilbert and Johnson, THIS JOURNAL, 51, 1526 (1929); Bass and Johnson, *ibid.*, 52, 1146 (1930).

[3] Harington, *Biochem.* J., 20,300 (1926); 22,1429 (1928); *C. A.*, 23, 1631 (1929).

[4] Johnson and Brautlecht, J. *Biol. Chem.*, 12,175 (1912).

its chemistry since that date. The further study of this interesting acid and its derivatives is now in progress.

The approach to α-amino acid derivatives of diaryl sulfides has been accomplished as a result of the successful introduction of aldehyde groups into sulfide-ether constructions. Previous to our work no aldehyde derivatives of an aromatic sulfide have been described in the chemical literature. Of the various procedures previously employed for introducing the aldehyde group into the aromatic nucleus,[5] the method of Stephen,[6] involving conversion of a nitrile to an imide by reduction, and the latter to an aldehyde by hydrolysis, was the only one considered at all practical for accomplishing our purpose. This was also the method utilized by Harington and Barger[7] in their original work leading to the final synthesis of thyroxine. There is a serious objection to the application of any oxidation process for aldehyde synthesis in this series of compounds, as we are dealing with sulfur constructions which are easily altered by application of such experimental technique. The sulfides represent the lowest valency state of sulfur **and** all reactions must be avoided which would tend to convert the respective sulfide to a sulfoxide or a sulfone. It now seems probable from the work already done in this Laboratory that the Stephen reaction will be found of quite general application for aldehyde synthesis in the aromatic sulfide series.

The starting points for our two amino acid syntheses were *p*-methyl-*p*′-cyandiphenyl-sulfide and *p*-ethoxy-*p*′-cyandiphenyl-sulfide expressed by formulas V and VI, respectively. These were transformed into the corresponding aldehydes, VII and VIII, by application of Stephen's reaction

$$\underset{\text{V}}{CH_3C_6H_4SC_6H_4CN} \qquad \underset{\text{VI}}{C_2H_5OC_6H_4SC_6H_4CN}$$

$$\underset{\text{VII}}{CH_3C_6H_4SC_6H_4CHO} \qquad \underset{\text{VIII}}{C_2H_5OC_6H_4SC_6H_4CHO}$$

and then condensed with hydantoin according to the method of Wheeler.[8] After reducing the resulting aldehyde condensation products, and then destroying the resulting hydantoin derivatives by alkaline hydrolysis, the corresponding a-amino acids were easily obtained in good yield. Dealkylation of *p*-ethoxy-*p*′-diphenylsulfide-β-alanine by heating with hydrobromic acid gave the sulfur analog of thyronine represented by formula II. Description of the products formed in the different stages of the two syntheses

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[5] Reimer–Tiemann method, *Ber.*, 9, 824 (1876); Gattermann, *Ann.*, 347, 347 (1906); *ibid.*, 357,313 (1907); Guyot, *Compt. rend.*, 149, 788 (1909); Bouveault, *ibid.*, 122, 1543 (1896); Gattermann and Maffezzoli, *Ber.*, 36, 4152 (1903); Bodroux, *Compt. rend.*, 138, 92, 700 (1904); Bouveault, *Bull. soc. chim.*, [III] 31, 1322 (1904); Étard, *Ann. chim.*, 22,218 (1881); Rosenmund, *Ber.*, 51,585 (1918).

[6] Stephen, *J. Chem. Soc.*, 127, 1874 (1925).

[7] Harington and Barger, *Biochem. J.*, 21, 169 (1927).

[8] Wheeler and Hoffman, *Am. Chem. J.*, 45,368 (1911).

are given in the experimental part of this paper. Further work dealing with the preparation and study of halogen derivatives of aromatic sulfide amino acids is now in progress.

Experimental Part

p-Ethoxythiophenol, $C_2H_5OC_6H_4SH$.—This thiophenol has previously been prepared by Lagai[9] and also Gattermann.[10] By application of the technique of Leuckart[11] we succeeded in preparing the same compound in good yield (77%) from *p*-phenetidine. Ninety-six grams of the amine is productive of 83–85 g. of the thiophenol distilling between 238–241".

p-Ethoxy-p^1-nitrodiphenyl-sulfide, $C_2H_5OC_6H_4SC_6H_4NO_2$.—This is formed by digesting in alcoholic solution the sodium salt of p-ethoxythiophenol with *p*-nitrochlorobenzene. The sulfide is easily obtained in a yield of 93% of the theoretical and crystallizes from alcohol in needles melting at 96". It is insoluble in water but soluble in all common organic solvents except petroleum ether.

Anal. Calcd. for $C_{14}H_{13}NSO_3$: N, 5.09; S, 11.63 Found: N, 4.90; S, 11.49.

p-Methyl-p'-nitrodiphenyl-sulfide, $CH_3C_6H_4SC_6H_4NO_2$, is obtained from *p*-thiocresol and p-nitrochlorobenzene in a yield of 95% of the theoretical. It crystallizes from alcohol in yellow needles melting at 81.5".

Anal. Calcd. for $C_{13}H_{11}O_2NS$: N, 5.71; S, 12 06. Found: N, 5.63; S, 13.12.

Reduction of these two nitro compounds with stannous chloride in dilute alcohol solution acidified with hydrochloric acid leads to the formation of the corresponding amino derivatives.

***p*-Ethoxy-*p'*-aminodiphenyl-sulfide,** melting at 53° from alcohol. The hydrochloride melts at 184–185°.

Anal. Calcd. for $C_{14}H_{15}ONS$: N, 5.71; S, 13.06 Found: N, 5.47; S, 13.01.

***p*-Methyl-*p'*-aminodiphenyl-sulfide,** melting at 73.5° from alcohol. The hydrochloride melts at 183–184° and is obtained in a yield of 84% of the theoretical.

Anal. Calcd. for $C_{13}H_{13}NS$: N, 6.51; S, 14.88. Found: N, 6.39; S, 15.01.

p-Ethoxy-p^1-cyandiphenyl-sulfide. **VI.**—From the corresponding amine by application of Sandmeyer's reaction. This was purified by distillation under diminished pressure and finally by crystallization from dilute acetic acid. It separated in colorless prisms melting at 95–96°. The nitrile is insoluble in water, but soluble in all the common organic solvents.

Anal. Calcd. for $C_{15}H_{13}ONS$: N, 5.49; S, 12.55. Found: N, 5.45; S, 12 39.

***p*-Methyl-*p'*-cyandiphenyl-sulfide. V.**—This was prepared from *p*-aminobenzonitrile[12] and *p*-thiocresol according to Ziegler's technique,[13] and also from *p*-methyl-*p'*-aminodiphenylsulfide by application of Sandmeyer's reaction. The yield by either method is about 45% of the theoretical. This nitrile is easily purified by crystallization from dilute acetic acid and crystallizes in plates melting at 102–103°.

Anal. Calcd. for $C_{14}H_{11}NS$: N, 6.22; S, 14.22. Found: N, 6.14; S, 14.08.

p-Ethoxy-diphenyl-sulfide-p^1-carboxylic acid, melts at 201–202° (calcd.: S, 11.68. Found: S, 11.75).

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[9] Lagai, *Ber.*, 25, 1838 (1892).

[10] Gattermann, *ibid.*, 32, 1149 (1899).

[11] Leuckart, *J. prakt. Chem.*, 41, 179 (1890).

[12] Bogert and Wise, THIS JOURNAL, 32, 1494 (1910).

[13] Ziegler, Ber., 23, 2471 (1890).

_p_-Methyl-diphenyl-sulfide-_p_'-carboxylic acid, melts at 197–198° (calcd.: S, 13.12. Found: S, 13.21).

_p_-Ethoxy-_p_'-aldehyde-diphenyl-sulfide. VIII.—Thirty grams of anhydrous stannous chloride is added to 900 cc. of dry ether and the solvent saturated at low temperature with hydrochloric acid gas. Eight grams of *p*-ethoxy-*p*'-cyandiphenyl-sulfide dissolved in 30 cc. of chloroform is then added and after thorough mixing the solution is allowed to stand in an ice chest for several hours. Saturation with hydrochloric acid gas is then repeated and the mixture again allowed to stand for eight to ten hours. The imide hydrochloride is then separated by filtration and immediately converted to the aldehyde by warming with very dilute hydrochloric acid solution. The aldehyde crystallizes from dilute acetic acid in plates which melt at 83°. It is insoluble in water, but soluble in all the common organic solvents.

Anal. Calcd. for $C_{15}H_{14}O_2S$: S, 12.41. Found: S, 12.42.

Its phenylhydrazone, $C_{21}H_{20}ON_2S$, crystallizes from alcohol in yellow needles melting at 126–127° (calcd.: N, 8.04. Found: N, 7.82).

_p_-Methyl-_p_'-aldehyde-diphenyl-sulfide. VII.—This is obtained from *p*-methyl-*p*'-cyandiphenyl-sulfide by application of Stephen's reaction in a yield of 81% of the theoretical. The aldehyde is purified by crystallization from dilute acetic acid and separates in plates melting at 69°.

Anal. Calcd. for $C_{14}H_{12}OS$: S, 14.04. Found: S, 14.17.

Its phenylhydrazone, $C_{20}H_{18}N_2S$, crystallizes from alcohol in yellow plates melting at 149–150° (calcd.: N, 8.80. Found: N, 8.61).

_p_-Methyl-diphenylsulfide-_p_'-aldal-hydantoin, $CH_3C_6H_4SC_6H_4CH{=}\overline{CCONHCONH}$.—This is formed in a yield of 71% of the theoretical by interaction of *p*-methyl-*p*'-aldehydodiphenyl-sulfide (15.5 g.) with hydantoin (6.9 g.) and sodium acetate (26 g.) in a mixture of glacial acetic and acetic anhydride heated at its boiling point for eight hours. On pouring into cold water the hydantoin separates and is purified by crystallization from dilute alcohol. It melts at 239–240° and is insoluble in water and ether and only sparingly soluble in alcohol and acetic acid.

Anal. Calcd. for $C_{17}H_{14}O_2N_2S$: N, 9.03; S, 10.32. Found: N, 8.83; S, 10.19.

_p_-Ethoxy-diphenyl-sulfide-_p_'-aldal-hydantoin, $C_2H_5OC_6H_4SC_6H_4CH{=}\overline{CCONHCONH}$.—This hydantoin crystallizes from dilute alcohol in needles which melt at 254° with decomposition. The hydantoin is insoluble in water and ether and only sparingly soluble in alcohol and acetic acid.

Anal. Calcd. for $C_{18}H_{16}O_3N_2S$: N, 8.24; S, 9.41. Found: N, 8.16; S, 9.22.

Reduction of **the** Unsaturated **Hydantoins.**—This was accomplished by dissolving the respective hydantoin in warm alcohol and then reducing it at the double bond by slow addition of 2.5% sodium amalgam to the solution. When the reduction was complete the solution was acidified with hydrochloric acid and the reduced hydantoin precipitated by addition of water. The yield of crude hydantoin is about 85–90% of the theoretical.

_p_-Methyl-diphenyl-sulfide-_p_'-aldyl-hydantoin, $CH_3C_6H_4SC_6H_4CH_2\overline{CHCONHCONH}$, crystallizes from dilute alcohol in plates which melt at 187–189°. It is insoluble in water and ether, and soluble in acetic acids.

Anal. Calcd. for $C_{17}H_{16}O_2N_2S$: N, 8.97; S, 10.25. Found: N, 8.82; S, 10.09.

_p_-Ethoxy-diphenyl-sulfide-_p_'-aldyl-hydantoin, $C_2H_5OC_6H_4SC_6H_4CH_2\overline{CHCONHCONH}$, crystallizes from dilute alcohol in needles which melt at 184–185°. It is insoluble in water and ether, but soluble in the common organic solvents.

Anal. Calcd. for $C_{18}H_{18}O_3N_2S$: N, **8.18**; S, 9.36. Found: **N, 8.09; S, 9.45.**

p-Methyl-p′-diphenyl-sulfide-β-alanine. I.—This a-amino acid is formed by heating its hydantoin (above] in strong aqueous barium hydroxide at the boiling point of the solution for several hours (forty-eight). On acidifying the alkaline solution with hydrochloric acid and cooling, the hydrochloride of the amino acid separated as clusters of colorless prismatic crystals. The yield was **81% of** the theoretical and the salt melted at 205–207° with decomposition. The free amino acid was precipitated from an aqueous solution of its hydrochloride by addition of sodium acetate. This proved to be a very insoluble substance, and was purified by repeatedly dissolving in alkaline solution and precipitating with acetic acid. The sodium salt was found to crystallize from dilute sodium hydroxide solution as needles. The acid gives the normal ninhydrin test characteristic of a-amino acids. The acid melts at 198–200° with great decomposition.

Anal. Calcd. for $C_{16}H_{17}O_2NS$: N, **4.88**; S, **11.15.** Found: N, **4.80**; S, **11.74.**

p-Ethoxy-p′-diphenyl-sulfide-β-alanine, $C_2H_5OC_6H_4SC_6H_4CH_2CH(NH_2)COOH$.—This is formed by hydrolysis of its corresponding hydantoin (above) with barium hydroxide (heating at **100°** for forty-eight hours). The yield of hydrochloride was 82% of the theoretical, and it melted at 218–220° with decomposition. The free amino acid melts at 208–210° with intense decomposition and is slightly soluble in dilute solutions of mineral acids and alkali and insoluble in water. It responds to the ninhydrin test for α-amino acids.

Anal. Calcd. for $C_{17}H_{19}O_3NS$: N, 4.41; S, **10.09.** Found: N, 4.38; **S. 10.21.**

p-Hydroxy-p′-diphenyl-sulfide-β-alanine or **Thiothyronine. 11.—This** amino acid is formed by heating the corresponding ethyl ether with a mixture of 48% hydrobromic acid and acetic anhydride at 90° for several hours (forty-eight). The reaction mixture was then diluted with water and the hydrobromic acid neutralized by addition of sodium acetate using alizarine as an indicator. The amino acid separated at once and was further purified by dissolving in sodium hydroxide solution and precipitating with acetic acid. Further purification was effected by dissolving the amino acid in hydrochloric acid and reprecipitating by adding to the solution sodium acetate. This amino acid crystallizes in the form of colorless spherical crystals which darken when heated at **230"** and melt with decomposition at 240–242°. It is insoluble in cold water, very slightly soluble in hot water, and also sparingly soluble in dilute acid and alkaline solutions. It gives a positive ninhydrin test but does not give as distinct and decisive a Millon's test as tyrosine. This later color change is undoubtedly influenced by the presence of sulfur in the sulfide molecule.

Anal. Calcd. for $C_{15}H_{15}O_3NS$: C, **62.2**; H, **5.19**; N, **4.84.** Found: C, **62.0**; H, **5.26**; **N, 5.00.**

Summary

1. The Stephen reaction for preparing aldehydes from cyanides has been applied with success in the diaryl-sulfide series.

2. The two aldehydes $CH_3C_6H_4SC_6H_4CHO$ and $C_2H_5OC_6H_4SC_6H_4CHO$ condense smoothly with hydantoin, giving condensation products which can be transformed into characteristic a-amino acids.

3. Three new α-amino acids have been described, including thiothyronine, the sulfur analog of thyronine or desiodo-thyroxine.

4. The study of these amino acids and their halogen substitution products is being continued.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

ISOMERIC ALPHA,BETA-DIPHENYL-DELTA-KETONIC ACIDS. I[1]

BY S. AVERY AND G. C. JORGENSEN

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Introduction

α,β-Diphenylglutaric acids, the isomerism of which has been explained by Avery and Maclay,[2] have, in so far as their asymmetric carbon atoms are concerned, a structure similar to α,β-diphenyl-δ-ketonic acids, as the following comparison shows.

Glutaric acids $CO(OH)CH_2CH(C_6H_5)CH(C_6H_5)CO_2H$
Ketonic acids $CO(R)CH_2CH(C_6H_5)CH(C_6H_5)CO_2H$

It is to be anticipated, therefore, that a careful study of isomeric δ-ketonic acids will disclose many points of similarity between these compounds and the corresponding 8-carboxylic or glutaric acids. By analogy it should be possible to synthesize two optically inactive stereoisomers in the case of each ketonic acid. These acids should form two definite series of isomeric derivatives, as nitriles and esters. The preparation of such compounds would add convincing evidence of the correctness of the explanation of stereoisomerism in the glutaric series. Finally, as in the glutaric series, it should be possible to resolve each inactive acid into its optical isomers. The present paper, however, deals with inactive isomers only.

The study just outlined would naturally begin with isomeric α,β-diphenyl-y-acetylbutyric acids, but inasmuch as efforts to prepare acids of this composition were unsuccessful, owing to the active hydrogen atoms of the acetyl group, attention was turned to other derivatives.

By combining benzyl cyanide or an ester of phenylacetic acid with benzalpinacolone, one might expect to synthesize derivatives of isomeric α,β-diphenyl-γ-trimethylacetylbutyric acids. The experimental part of the paper will show that such compounds were easily formed in so far as the higher-melting series is concerned. Lower-melting isomers, however, were formed in small quantities. It was, moreover, not found possible to secure them free from isomeric admixture. The higher-melting series is as follows

$$\begin{tikzcd}
\text{Methyl ester } 175° \arrow[rd, shift left] & \\
& \text{Acid } 235\text{–}236° \arrow[lu, shift left] \\
\text{Nitrile } 86° \arrow[ru] &
\end{tikzcd}$$

The lower-melting series will be discussed in the experimental part of this paper.

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[1] Read at the Atlanta meeting, Organic Section, American Chemical Society, April 8, 1930.

[2] Avery and Maclay, THIS JOURNAL, 51,2833 (1929).

Owing to the poor yield and the doubtful purity of the lower-melting isomers, the authors of this paper decided to turn their attention to the corresponding benzoyl derivatives, which had already found a place in chemical literature.

The Isomeric α,β-Diphenyl-γ-benzoylbutyric Acids.—Borsche,[3] by combining ethyl phenylacetate with benzalacetophenone, obtained an ethyl ester of this series melting at 153–154° which hydrolyzed in alkaline solution to the salt of an acid melting at about 240°. He designated it as α,β-diphenyl-γ-benzoylbutyric acid.

By the oxidation of α,β,δ-triphenyl-δ-hydroxyvaleric acid, Meerwein[4] obtained an acid of the same composition melting at 186–187°. By combining methyl phenylacetate with benzalacetophenone, he obtained a mixture of isomeric esters. The esters yielded two acids, one melting at 186–187°, identical with the oxidation product previously obtained, and an isomer melting at 260–261°. These formed methyl esters melting at 157–158° and 177–178°, respectively. Meerwein's work indicates that the 240° acid of Borsche was a mixture of isomers.

By combining benzyl cyanide with benzalacetophenone, Kohler and Allen[5] obtained a nitrile melting at 118° and an isomer melting at 109'. The higher-melting nitrile gave a methyl ester melting at 150°, the lower nitrile a methyl ester melting at 139'. Both esters gave on saponification an acid melting at 239'. This acid on esterification with methanol and hydrogen chloride gave a product melting at 150°, identical with the ester (150") obtained directly from the higher-melting nitrile.

Owing to the lack of close agreement in certain parts of the work of previous investigators, the authors of this paper have attempted to clarify the subject by repeating (with some modifications) and extending the work of their predecessors. They have made free from isomeric admixture the ethyl ester (156° corr.) of Borsche, (1) by direct synthesis, (2) by esterification of the 260–261° acid of Meerwein and (3) by treating the 118° nitrile of Kohler and Allen with ethanol and hydrogen chloride. The methyl ester 177–178° of Meerwein has been prepared (1) by direct synthesis, (2) by treating the 118° nitrile with methanol and hydrogen chloride, and (3) by esterification of the 260–261° acid. The 260–261° acid of Meerwein has been prepared (1) by hydrolyzing the 156° ethyl ester, also the 177–178° methyl ester, (2) by hydrolyzing the 118° nitrile, and (3) by hydrolyzing a lactone not found in the literature of the subject.

The 186–187° acid of Meerwein has been prepared (1) by fractional crystallization from a mixture of the acids resulting from the hydrolysis of the mixed esters or of the mixed nitriles, (2) by hydrolysis of the pure

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[3] **Borsche,** *Ber.*, 42,4497 (1909).

[4] **Meerwein,** J. *prakt. Chem.*, 97,272 (1918).

[5] **Kohler** and **Allen,** THIS JOURNAL, 46, 1522 (1924).

esters (ethyl 100–101°, methyl 155°), and (3) by the hydrolysis of a lactone. The following list shows the members of both series that the authors of the present paper have prepared free from any isomeric admixture.

The higher-melting series

Methyl ester	177–178°	⇄	Acid 260–261°
Ethyl ester	156°	⇄	
Lactone	220–222°	⇄	
Nitrile	118°	→	

The lower-melting series

Methyl ester	155°	⇄	Acid 186–187°
Ethyl ester	100–101°	⇄	
Lactone	136°	⇄	

The ready formation of distinct lactones from both acids and the hydrolysis of these lactones into the original acids is evidence against the assumption of a "*trans*" or "fumaroid form for the 260–261° acid and the "cis" or "maleinoid" form for the 186–187° acid.

Experimental Part

The Trimethylacetyl Derivatives

The Nitrile of α,β-Diphenyl-γ-trimethylacetylbutyric Acid.—Benzalpinacolone condenses with benzyl cyanide readily under a variety of conditions. The details of the procedure employed will be given under the description of the condensation of benzyl cyanide with benzalacetophenone. No trimolecular body is formed. On recrystallizing from light gasoline, crystals superficially reminding one of quartz are obtained, melting point 86° (corr.), yield about 90% of the theoretical.

Anal. Calcd. for $C_{21}H_{23}NO$: C, 82.57; H, 7.60; N, 4.62. Found: C, 82.57; H, 7.84; N, 4.50.

The 86° nitrile hydrolyzed (in acid solution) to an acid melting at 236°, while a less pure sample, of slightly lower and less definite melting point, not only gave the 236° acid but also a small percentage of an acid melting between 189 and 190°.

The Methyl Ester of α,β-Diphenyl-γ-trimethylacetylbutyric Acid.—A crystalline mass is formed by the reaction of benzalpinacolone with methyl phenylacetate in the presence of sodium methylate. The yield of the impure ester was nearly quantitative. Repeated recrystallizations from methanol gave a product forming long slender needles melting at 175°, soluble in chloroform and benzene.

Anal. Calcd. for $C_{22}H_{26}O_3$: C, 78.06; H, 7.75. Found: C, 77.97; H, 7.78.

The ester saponified (in acid solution) to an acid identical with the 236° acid obtained from the nitrile. The 236" acid with methanol and hydrogen chloride again formed the 175° ester.

The filtrates from the above were condensed and again recrystallized from methanol. By repeated fractional crystallizations a small amount of a product forming long, slender rods, m. p. 110–115°, was obtained. It was found impossible to obtain a product with a sharp melting point.

Anal. Calcd. for $C_{22}H_{26}O_3$: C, 78.06; H, 7.75. Found: C, 77.64; H, 7.70.

This 110–115° ester saponified in acid solution to a 189–190° melting acid.

The α,β-Diphenyl-γ-trimethylacetylbutyric Acid.—As previously stated, a sharply melting acid may be prepared from the 86° nitrile or the 175° methyl ester by hydrolysis in acid solution. This 236° acid crystallizes from 95% ethyl alcohol in flattened needles or long plates.

Titration. 0.3211 g. required 19.72 cc. of $N/10$ NaOH. Calcd.: 19.82 cc. ***Anal.*** Calcd. for $C_{21}H_{24}O_3$: C, 77.73; H, 7.46. Found: C, 77.76; H, 7.43.

The evidently impure 110–115° ester saponified to an acid melting at 189–190°. A sharp melting point could not be obtained after repeated recrystallizations of the small amount available. It appeared to be identical with the acid obtained from the fraction of the nitrile melting below 86°.

Titration. 0.3904 g. required 24.16 cc. of $N/20$ NaOH. Calcd.: 24.10 cc. ***Anal.*** Calcd. for $C_{21}H_{24}O_3$: C, 77.73; H, 7.46. Found: C, 77.63; H, 7.46

In spite of the analytical data, the presence of the lower-melting isomers is not definitely established. The quantities were minute in comparison with the well-defined bodies of a higher-melting series. Sharp melting points and clearly defined crystal forms are lacking. The most probable conclusion is that the 110–115° ester and the 189–190° acid, though members of a lower-melting series, contain also a small admixture of the higher isomers and possible traces of some unidentified compound.

The above view is further strengthened by the fact that when the pure 175° ester is saponified in alkaline solution, the salts of mired acids are formed. From this mixture the pure 236° acid, and an acid or acid mixture melting at 189–190° can be separated by fractional crystallization. The change from the pure ester to a mixture of isomeric acid salts by hydrolysis in alkaline solution will be dealt with later in this paper.

An attempt was made to obtain the lower-melting acid in pure condition by proceeding in the following manner. Phenylacetaldehyde was united to benzalpinacolone in the presence of sodium methylate. A product melting sharply at 158°, of very definite crystalline character was obtained. The composition is that of a direct addition product, $C_{21}H_{24}O_2$. This substance proved to be highly stable, thus differing in behavior from the α,β,δ-triphenylvalerolactone of Meerwein.

The Benzoyl Derivatives

Preparation of the 118° Nitrile of α,β-Diphenyl-γ-benzoylbutyric Acid.—A yield of nearly 90% of this compound (melting at 116–118°) was obtained by slightly modifying the procedure of Kohler and Allen. On the basis of the benzalacetophenone employed, about a 10% excess of benzyl cyanide was used and less than one mole of sodium methylate in a methanol solution. The mixture was stirred for half an hour at the temperature of the ice-bath, then at room temperature. After seeding with nitrile previously prepared, a crystalline mass separated out which soon became too thick to stir conveniently. Ligroin was then added and stirring continued. After two hours of vigorous stirring, glacial acetic acid in slight excess in proportion to the sodium methylate was added and the mass filtered off, washed with ligroin, dried and recrystallized. Made in this way it is nearly free from the trimolecular body and from the lower-melting nitrile of Kohler and Allen. This last named compound, thoroughly investigated by these authors, was prepared in this Laboratory in quantity and purity sufficient only to show its relation to the 186–187° acid.

Hydrolysis of the Nitriles.—The nitrile is dissolved in boiling acetic acid in a flask fitted with a return flow condenser. To the boiling solution, drop by drop, a mixture of equal volumes of sulfuric acid and water is added. Separation of oily drops of the unchanged nitrile indicates that the strong aqueous sulfuric acid solution is being added too rapidly. After some time crystals begin to appear in the boiling solution. During a period of about six hours, the original acetic acid solution is diluted to about two volumes with the sulfuric acid solution.

The content of the flask is now poured into cold water and filtered. The crystalline substance retained by the filter is treated in a large beaker with potassium carbonate, in slight excess, dissolved in enough boiling water to hold in solution the difficultly soluble potassium salt formed. The undissolved portion is unchanged nitrile and a small amount of an unidentified cleavage product. This is filtered off and rejected. The filtrate contains the acid sought in the form of the potassium salt, which being difficultly soluble in water may partially separate out on cooling. The filtrate is acidified, the precipitated acid filtered off, dried and recrystallized using methods described under the next sub-heading.

Hydrolyzed in the above manner, the 118" nitrile yields the 260–261° acid. The lower-melting nitrile gives the 186–187° acid. Hydrolyzing in acid solution is of importance inasmuch as many nitriles cannot be successfully saponified by sodium or potassium hydroxides and, further, as previously pointed out by Avery and Maclay for the glutaric series, hydrolyzing in an acid medium at moderate temperature does not effect a transformation of the lower $\rightleftarrows$ higher series, while the sodium or potassium hydroxides often cause such transformation.

Preparation of the Mixed (260–261° and 186–187°) α,β-Diphenyl-γ-benzoylbutyric Acids.—Ten and four-tenths grams of benzalacetophenone and 7.5 g. of methyl phenylacetate were dissolved in 25 cc. of absolute methanol. To the solution, cooled in an ice-bath, 1.15 g. of sodium dissolved in absolute methanol was added. The mixture was stirred for half an hour in the ice-bath and then at room temperature until it was too thick to stir well. Ligroin was added as a diluent and stirring continued for several hours; 5 cc. of glacial acetic acid was added and the stirring continued for half an hour. The crystalline mass was filtered, washed with ligroin and dried. The mixed esters were then hydrolyzed in acid solution and the mixed acids separated as follows. The 260–261° acid separated out on cooling from a hot glacial acetic solution of the two acids and is obtained in a pure condition by further recrystallization from this solvent. The acetic acid filtrates are brought together, heated and water added until a crystallizing precipitate forms at the boiling temperature. On cooling, nearly all of the 186–187" acid separates out. By fractional recrystallization from hot benzene, rejecting the small portion of the 260–261° acid that first separates out on cooling, the acid is obtained in a nearly pure condition. Recrystallization again from benzene gives the pure 186–187° acid. This is an adaptation of the procedure of Borsche and of Meerwein.

The Ethyl Ester of the 186–187° Acid.—To complete the series of methyl and ethyl esters (for both isomers) the ethyl ester of the lower-melting acid was prepared with ethyl alcohol and hydrochloric acid. It is readily soluble in the usual organic solvents, crystallizes in long, slender plates or needles and melts at 100.5°.

The Lactones of the α,β-Diphenyl-γ-benzoylbutyric Acids.—The 186–187° acid dissolves readily in acetyl chloride at the temperature of the steam-bath. The concentrated solution is treated with ligroin and the precipitate formed recrystallized from tertiary amyl alcohol. It separates from this solvent as needles or long prisms, soluble in acetic acid, chloroform and benzene, m. p. 136°. On heating the solution in acetic acid to boiling, adding 50% sulfuric acid and continuing the boiling for a few minutes, the 186–187" acid is regenerated.

The 260–261° acid is less readily soluble in acetyl chloride. The lactone begins to separate out before the acid is completely dissolved. After protracted boiling, ligroin is added to the flask containing the products of the reaction and the mass is filtered off and recrystallized out of a mixture of tertiary amyl alcohol and chloroform. It forms needles or rods, more difficultly soluble in the ordinary solvents than its isomer, m. p. 220–222°. It hydrolyzes to the 260–261° acid.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.62; H, 5.56. Found for the 136° lactone: C, 84.30; H, 5.60. Found for the 220–222° lactone: C, 84.48; H, 5.64,

Transformation: The Higher Series ⇄ the Lower.—Saponification by alcoholic potassium or sodium hydroxide of the esters of either series leads to the corresponding acid, mixed, however, with a certain amount of the isomer. The action appears to explain why in some previous investigations an acid melting at 239–240° was obtained.

Summary

The points of analogy between the corresponding 8-ketonic and δ-carboxylic acids are considered.

α,β-Diphenyl-γ-trimethylacetylbutyric acid has been synthesized and possible isomeric forms are discussed.

The work of previous investigators on α,β-diphenyl-γ-benzoylbutyric acid is reviewed. Discrepancies in the literature are found to have resulted mainly from the hydrolysis of pure esters by sodium or potassium hydroxide, thus forming isomeric mixtures. Through the preparation of new compounds, both series of the isomeric benzoyl derivatives are now fairly complete. Resolution of both isomeric acids into optical isomers may be anticipated.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NORTH DAKOTA]

ACTION OF METALLIC SODIUM ON DIPHENYL- AND DITOLYLTRICHLORO-ETHANES[1]

BY ELWIN E. HARRIS

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In a former report[2] the author stated that when diphenetyltrichloroethane was treated wuth sodium in benzene a good yield of *p,p'*-diethoxystilbene was obtained. He was unable at the time to account for the mechanism of the reaction although similar products had been reported from the reaction of the same compound with zinc.[3] This investigation was undertaken to determine the course of the reaction and the nature of the products formed.

It was found that the presence of moisture is essential to the reaction in benzene, as in its absence no *p,p'*-diethoxystilbene could be isolated and most of the starting product was recovered unchanged. The reaction apparently takes the course

$$(C_2H_5OC_6H_4)_2CHCCl_3 + 4Na + H_2O \longrightarrow C_2H_5OC_6H_4CH{=}CHC_6H_4OC_2H_5 + 3NaCl + NaOH$$

Fritsch[4] found that heating the compound with sodium alcoholate in a

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[1] The author was assisted in this work by Irma Magnusson, graduate assistant in chemistry at the University of North Dakota.

[2] Harris and Frankforter, THIS JOURNAL, **48,** 3144 (1926).

[3] Goldschmidt, *Ber.*, 6, 990 (1874); Elbs and Foster, *J. prakt. Chem.*, 39,298 (1882).

[4] Fritsch and Feldmann, *Ann.*, 306, 72 (1899).

sealed tube for six hours gave a good yield of the stilbene. To keep the sodium melted and to raise the temperature, toluene was substituted for the benzene. Precautions were taken to prevent moisture from entering the apparatus and all the chemicals were carefully dried. A very violent reaction took place which in a few cases was uncontrollable and a fire resulted. The mixture became deep greenish-brown in color. The reaction was so complex and so many-products were formed that further work was postponed on diphenetyltrichloro-ethane and ditolyltrichloro-ethane was substituted in the study. The same kind of reaction resulted except that it was much less violent. About 50% of the starting product could be accounted for as *p,p*-dimethylstilbene and about 45% as pip-dimethyltolane. The equation is

$$2(CH_3C_6H_4)_2CHCCl_3 + 3Na \longrightarrow CH_3C_6H_4CH{=}CHC_6H_4CH_3 + CH_3C_6H_4C{\equiv}CC_6H_4CH_3 + 3NaCl$$

It is obvious that rearrangement and intramolecular oxidation have taken place. Other studies on this interesting reaction are now in progress.

Experimental Part

Apparatus and Materials.—The apparatus used was a round-bottomed flask fitted with a dropping funnel, a mercury-sealed stirrer and a reflux condenser. To give plenty of room for possible frothing, the Bask had a capacity ten times the volume of the contents. The dropping funnel and the condenser were fitted with drying tubes.

The toluene was treated first with a small amount of sulfuric acid, washed with water and 10% sodium hydroxide, then dried over calcium chloride and finally allowed to stand over sodium powder for a week or more. It was then distilled from fresh sodium with a distilling tube. Only that portion boiling from 110 to 112° was used, and this was caught in the flask to be used for the experiment. The sodium was the commercial purified form. The crust was removed under toluene and the sodium transferred quickly to the reaction flask. The diphenyl- and the ditolyltrichloro-ethanes were prepared according to the method formerly described by the author.[2] These were recrystallized from toluene just before the experiment.

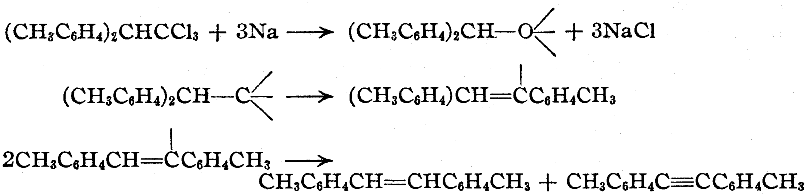
Observations

The Action of Sodium on **β,β,-Ditolyl-α,α,α-trichloro-ethane** in Boiling Toluene.—Thirty-one grams of ditolyltrichloro-ethane was dissolved in 150 cc. of the purified toluene and placed in the dropping funnel, which was kept warm with a hot cloth, and allowed to drop onto 14 g. of melted sodium in boiling toluene. It was stirred with an electric stirrer to keep the sodium whipped to a very fine powder. A violent reaction began almost immediately and lasted for about twenty minutes. The mixture turned green. It was then heated for an hour with continuous stirring. The sodium was allowed to settle and the toluene solution was decanted off. The sodium was extracted several times with more hot toluene and finally treated with alcohol. No organic product was found in the alcoholic solution from the sodium. The toluene solution was concentrated and cooled. *p,p'*-Dimethylstilbene crystallized out in large plates. These were filtered off and recrystallized from benzene, melting point 177°; dibromide, melting point 214°. The filtrate was again concentrated and another crop of the substituted stilbene separated. The combined portions represented over 45% yield from the starting product. Alcohol was then added to the filtrate from the stilbene and there separated *p,p'*-dimethyltolane and a yellow compound which did not melt sharply; m. p. 85 to 90°. It was very soluble in benzene, and more soluble in alcohol than the stilbene or the tolane. Each crystallization of this yellow compound gave a small amount of *p,p'*-dimethyltolane melting at 135°; dibromide, 204°. The addition of a small amount of hydrochloric acid to the alcohol from which it was crystallized caused all of the yellow compound to change to the tolane. One sample of the yellow compound stood in a tube for four years and was found to have changed over to the tolane, melting at 135°. These combined portions of the tolane brought the yield to about 45%, accounting for 90 to 95% of the starting material.

The Action of Sodium on **β,β-Diphenyl-α,α,α-trichloro-ethane.**—The reaction described above was performed with diphenyltrichloro-ethane. In all respects it seemed to be much the same as that above, but it has been very difficult to isolate the products formed. Some of each of the following were found, and converted into their dibromide for identification: normal stilbene melting at 124° (dibromide, 236°); isostilbene, an oil (dibromide, 109°) and tolane, melting point 60° (tolane dibromide, 208°). Although it was impossible to obtain very large portions of the above compounds from the reaction. no other products were found; therefore one would be led to believe that the mechanism of the reaction was the same as in the first case.

Attempts to Isolate Intermediate Sodium Compounds.—The above reactions were also run in an atmosphere of nitrogen to eliminate the effect of air on the reaction, which may decompose any sodium organic complex. Carbon dioxide was then passed into the mixture but there was no indication of a reaction to form the acid derivative of tolane or stilbene.

Mechanism of the Reaction.—The formation of an intermediate sodium compound would be a simpler method of accounting for the reaction, but since none could be found, it should not be used in interpreting the reaction. The mechanism given below is similar to one given by Wooster.[5]



$$(CH_3C_6H_4)_2CHCCl_3 + 3Na \longrightarrow (CH_3C_6H_4)_2CH-O\lt + 3NaCl \qquad (1)$$

$$(CH_3C_6H_4)_2CH-C\lt \longrightarrow (CH_3C_6H_4)CH=\overset{|}{C}C_6H_4CH_3 \qquad (2)$$

$$2CH_3C_6H_4CH=\overset{|}{C}C_6H_4CH_3 \longrightarrow CH_3C_6H_4CH=CHC_6H_4CH_3 + CH_3C_6H_4C\equiv CC_6H_4CH_3 \qquad (3)$$

The second equation should easily form a dimolecular compound. If such a dimolecular compound was formed, it must have split immediately, with rearrangement to form stilbene and tolanes. This wandering of groups is similar to that shown by Lachman,[6] also by Stieglitz[7] and Tiffeneau.[8] This reaction is not preceded by the elimination of hydrogen chloride, as was suggested in the reaction by Wooster,[5] for this would give rise to compounds in which the ethane hydrogen is absent. A study of a reaction in which the hydrogen chloride is first removed is to be the subject of another report.

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[5] Wooster, THIS JOURNAL, 52, 1045 (1930).

[6] Lachman, *ibid.*, 44,330 (1922); 45,1509 (1923).

[7] Stieglitz, *ibid.*, 36, 272 (1914).

[8] Tiffeneau, Rw. *Gsn. Sci. pur et appl.*, 583 (1907).

Summary

1. The action of sodium on ditolyltrichloro-ethane in boiling toluene results in the formation of *p,p'*-dimethylstilbene and *p,p'*-dimethyltolane.

2. A similar reaction takes place when sodium acts on diphenyltrichloro-ethane.

3. A possible interpretation of the reaction is given, involving the formation of monovalent carbon followed by the rearrangement of the phenyl groups within the molecule and the redistribution of the hydrogens between the molecules.

GRAND FORKS, NORTH DAKOTA

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

THE POLYHYDRIC ALCOHOL–POLYBASIC ACID REACTION.

II. ETHYLENE GLYCOL–PHTHALIC ANHYDRIDE

BY R. H. KIENLE AND A. G. HOVEY

RECEIVED MAY 24, 1930 PUBLISHED SEPTEMBER 5, 1930

Introduction

In the first paper of this series[1] the reaction between glycerol and phthalic anhydride was described. The changes in properties were shown to be gradual and continuous. The conclusion was drawn that although the reaction proceeded by esterification, it did not necessarily take place with the formation of definite mono-, di- or triglycerides, but that a heterogeneous complexity of esters resulted.

It is interesting to compare the reaction of ethylene glycol and phthalic anhydride with the reaction of glycerol and the same acid, for ethylene glycol is a smaller and simpler molecule than glycerol. Any differences in properties of the resinous products of the reactions should therefore be due to the difference in size and structure of the alcohols.

Historical.—The reaction of ethylene glycol with phthalic anhydride was known to M. J. Callahan[2] in 1914, but the resin did not receive commercial application as soon as that formed from the glycerol–phthalic anhydride reaction, because ethylene glycol has not been available in considerable quantities until within the last five or six years. Much additional work was done by J. G. E. Wright and co-workers, the authors, and others, with the result that certain modifications of the reaction have been effected and several novel resins of commercial value have been produced. Recently, R. H. Kienle and C. S. Ferguson[3] described the product of the ethylene glycol–phthalic anhydride reaction as belonging to a "heat-

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[1] R. H. Kienle and A. G. Hovey, THIS JOURNAL, 51,509 (1929).

[2] M. J. Callahan, unpublished data and such patents as U. S. Patents 1,091,627, 1,091,628 and 1,091,732.

[3] R. H. Kienle and C. S. Ferguson, Ind. Eng. Chem., 21,399 (1929).

non-convertible" type of film-forming resins. Carothers and Arvin[4] gave a description of methods of preparing glycol phthalate esters and obtained their molecular weights.

Materials.—C. P. phthalic anhydride (Monsanto Chemical Co.) having a melting point of 131.1°, and ethylene glycol of the best grade furnished by Carbide and Carbon Chemicals Corporation, having a specific gravity of 1.069 and boiling point of 194°, were used.

Experimental Part

I. A Study of the Products of the Reaction.—In the first paper of this series[1] the products of the glycerol–phthalic anhydride reaction were studied and found to be nothing more than water and resin. It was concluded that the only reaction involved was that of esterification. A similar result was obtained for the glycol–phthalic anhydride reaction.

Using an apparatus as described in our previous paper, the reaction mixture was heated in a tared Erlenmeyer flask on a sand-bath. To prevent oxidation, a stream of nitrogen carried the vapors evolved through Traps A, B and C where solid, liquid and gas were collected, respectively, and then finally through Trap D which contained a solution of rosaniline and sulfurous acid to detect any volatile aldehyde or reducing compounds which might not condense in the liquid-air trap if blown through too rapidly.

Stoichiometrical proportions (186 g. of ethylene glycol and 444 g. of phthalic anhydride) were gradually heated from room temperature to 230°. At this temperature the mix was maintained for three and one-quarter hours, when it seemed that a final equilibrium had been reached. Unlike the resinous product of the glycerol–phthalic anhydride reaction, no gelation takes place, so there is no way of knowing how far the reaction has gone except by taking out some of the reaction mixture and testing it. After cooling, the reaction mixture was found to consist of a clear, transparent, brittle resin (yield 568 g.) having the following characteristics: flow point, 69°; acid number, 22.8; saponification number, 582.8; (calcd.) percentage of esterification, 96.5%.

The traps A, B and C were disconnected and weighed. The total amount of material collected was 62.0 g., which agreed with the loss in weight of the reaction mixture. The amount of phthalic anhydride in each trap was found by titration with standard potassium hydroxide solution using phenolphthalein as an indicator. The samples were then made acid and tested for the presence of aldehydes using a standard rosaniline–sulfurous acid solution,[5] shaking and allowing to stand overnight.

Table I shows the results obtained upon examining the products collected in the various traps. As in the case of the glycerol reaction, the amount of phthalic anhydride evolved is far less than would be expected from watching the reaction take place. Most of the material in each trap was a clear transparent liquid with melting point approximately zero. Making due allowance for the effect of varying quantities of dissolved phthalic anhydride on the melting points of the liquids, nothing but phthalic anhydride, glycol and water were found. A determination of the amount of glycol distilled over was not made.

The tests for aldehyde were so weak that it is very doubtful whether any

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[4] W. H. Carothers and J. A. Arvin, THIS JOURNAL, 51, 2568 (1929).

[5] Allen, "Commercial Organic Analysis," 5th ed., Vol. I, p. 324.

Table I

Results of Experiments

Trap no.	A	B	C	D	Total
Material coll., g.	52.1	3.8	6.1	...	62.0
0.0874 N KOH, cc.	149.42	1.78	14.36	...	166.56
Equiv. wt. of phthalic anhyd., g.	0.968	0.012	0.094	...	1.074
Obs. m. p., °C.	......	0.2	Almost exactly zero		......
Aldehyde test	Very doubtful	None	Very weak test only at very last stage of the reaction	None	No aldehyde found in the reaction mixture itself
Odor	Burnt sugar	Burnt sugar	Burnt glycerol	...	
Remarks	Detn. of amt. of glycol distilled not made	Diff. in m. p. from product in Trap C thought to be due to glycol	Phthalic anhydride present both as crystals and in solution	...,	Inferred that water and resin are only products. Some phthalic anhydride and glycol distilled over

reducing substances were present at all. Judging by the amount of coloration when a known amount of acrolein was added to the rosaniline solution, there could not have been a total of 0.1 g. of aldehyde present in all three traps. No volatile aldehyde was found escaping the liquid-air trap C. No aldehyde was detected in the reaction mixture itself.

Since aldehyde, if present at all, is in so small a proportion that it can scarcely be detected, it is very doubtful whether the mechanism by which resins are formed from glycol and phthalic anhydride is through the formation of an intermediate aldehyde. The only products of the reaction seem to be water and resinous esters, and since the reacting molecules are those of an alcohol and of an acid, it is highly probable that the reaction is that of esterification.

II. Kinetic Isothermal Studies with Time.—As in the case of the reaction of glycerol with phthalic anhydride, this reaction was followed by determining the change of the free acid and of the combined acid with time.

Preparation of Samples.—The reaction was allowed to proceed at atmospheric pressure, keeping the conditions as nearly isothermal as possible, while **124** g. of the ethylene glycol was weighed out into the reaction vessel and heated up to its boiling point, phthalic anhydride was heated in an Erlenmeyer flask slightly above the temperature at which the reaction was to take place to allow for the cooling effect of pouring. When ready to start the reaction, **396** g. of the molten phthalic anhydride was weighed out into the reaction vessel and stirred up with the glycol. Because of the rapid progress of the reaction at the start, so much heat is evolved in a short time that the temperature of the reaction mixture rapidly rises about 40° above the temperature that it had at the instant of mixing. Since the boiling point of glycol is 197.5°, it was necessary to depend upon this quick rise in temperature when mixing the alcohol and acid in order to attain the isothermal conditions for the higher temperature runs.

If it was desired to run the reaction at lower temperatures, it was necessary to cool as rapidly as possible with a jet of compressed air until the right temperature was obtained. In either case, as soon as the desired temperature was reached, the reaction vessel was lowered into a constant temperature oil-bath and the reaction allowed to proceed to completion with the necessary amount of heat supplied to maintain isothermal conditions.

Samples of the reaction mixture were pipetted out from time to time and allowed to cool rapidly, thus freezing the equilibrium at that point. This was done oftener in the earlier stages than in the later stages, because the reaction was proceeding so much more rapidly. The viscosity of the liquid reaction mixture kept increasing as in the case of the glycerol–phthalic anhydride, but finally reached a maximum with no gelation taking place. Since gelation did not take place, it was possible to carry the reaction practically to completion.

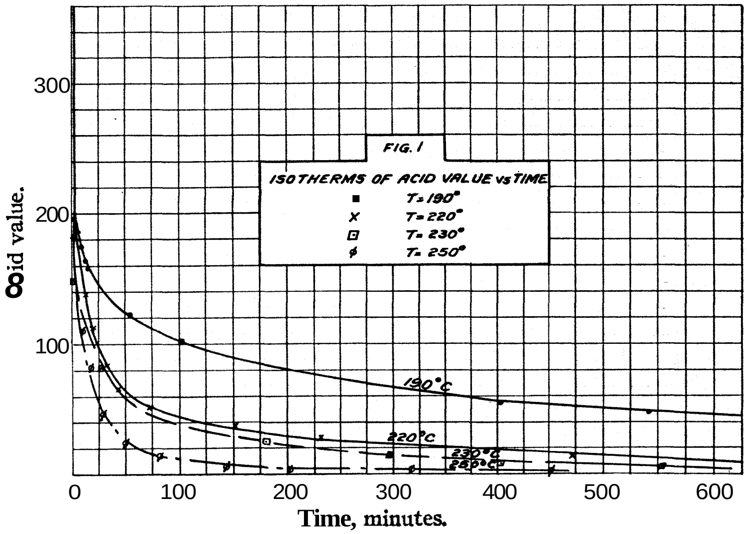


Fig. 1.

(a) Free Acidity.—The change in free acidity with time was determined and reported both as acid number and as percentage of free phthalic anhydride. Samples weighing 1 g. each were dissolved in 25 cc of C. P. acetone and titrated with 0.1 *N* potassium hydroxide solution using phenolphthalein as indicator.

As in the case of the glycerol–phthalic anhydride reaction, the free acidity is reduced to at least one-half within the first minute after mixing the hot liquids, after which it proceeds to completion at a greatly diminished rate. The graphical representation of the change in free acidity with time is shown in Fig. 1.

(b) Saponification Number.—The method of determining the saponification number differed from the procedure which was used in the first paper[1] in that the samples, after titration for free acidity, were used for the determination of ester number. The samples were refluxed for one hour with 50 cc. of normal alcoholic potassium hydroxide solution. Upon cooling, titration was effected with 0.5 N hydrochloric acid until the pink color of the phenolphthalein disappeared; then 0.5 N potassium hydroxide solution was run in until the pink color reappeared. The calculation of ester number was made from this titration, which added to the acid number gave the saponification number. Although the saponification number for zero time was calculated as 534.5, actually a lower value was obtained for the earliest time at which the reaction mixture could be sampled. Then as the reaction proceeded, the saponification number increased, finally reaching a more or less constant value. The observed variation in saponification number was probably due to the presence of water, and its subsequent evolution.

(c) Degree of **Esterification.**—The ratio of the amount of combined acid to the total amount of acid give's the degree of esterification—a measure of the completeness of the reaction. The change of this value with time is given in Fig. 2, which shows the rapid increase in esterification at the start of the reaction and the falling off in the rate of increase as the reaction approaches completion.

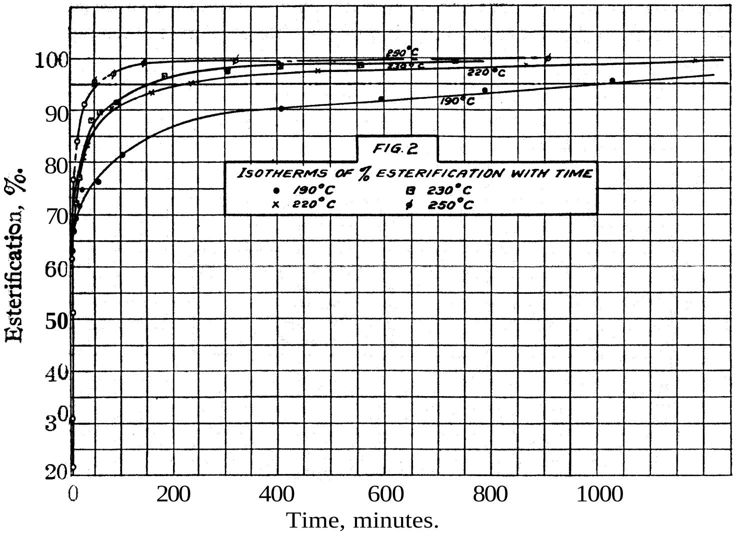


Fig 2.

(d) Variation of Other Properties with Time. 1. Flow Point.—The flow point[1] gradually increases as the reaction proceeds, as is shown in Fig. 3, and reaches a maximum of about 80° when the reaction is complete. Since no gelation takes place upon further heating, the flow point can always be taken, but has not been found to increase appreciably.

2. Viscosity.—The viscosity of the hot liquid reaction mixture increases, but when the esterification is complete, the viscosity appears to have reached a final value.

3. Density.—The density at 25.0–25.0° was determined using a pycnometer with specially distilled mineral spirits (sp. gr. 0.7779) as an inert liquid. The results are included in Table **II.** The variation of density with time is found to be quite irregular, although there is a definite upward trend throughout the reaction. The same type of variation has also been found, by careful check, to exist in the case of the resinous product of the reaction of phthalic anhydride and glycerol.[6]

4. Color.—The color change is even less than that of the glycerol–phthalic anhydride reaction. The resin is clear, colorless and transparent at the start and remains so up to the end, when it resembles glass.

An error has been found in our previous paper [THIS JOURNAL, 51, 509 (1929)]. In Table IIb the density data should read: time 3420 sec., d, 1.376; 3980 sec., d, 1.390; 5740 sec., d, 1.420; 9720 sec., d, 1.400.

5. Refractive Index.—The refractive index of the resinous product was found to be within the limits of 1.560 and 1.570.

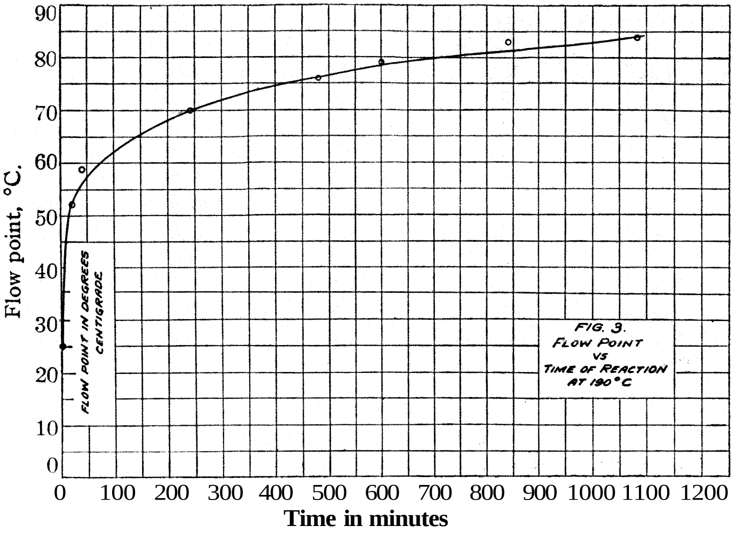


Fig 3

Table II shows a comparison of the variations of different properties of a set of standard samples taken from time to time with the temperature at 190°.

TABLE II

PROPERTIES OF SAMPLES (T, 190°)

Time, min.	Free acid, %[a]	Acid no	Ester no.	Sap. no.	Ester, %	Sp. gr.	Refr index
0	70.48	(534 5)		(534.5)	0	...	..
3	25.44	196	292	488	60	...	..
4	25.13	185	313	498	63	1.315	...
8	23.07	175	350	525	67	1.311	..
1225	21.47	1625	374	536	698	1.313	...
17.25	21.07	159 5	399	558	71.5	1.319	...
23 25	18 36	139	415	554	75 0	1.326	...
57	16.25	123	403	526	76.5	1.323	...
100	13.25	100.3	450	550	81.5	1.323	...
404	7.28	55	520	575	90 5	1 323	1 560
544	6.25	48	531	579	92.0	1.366	...
784	4.77	36.0	564	600	94.0	1.325	...
1024	384	29.0	570	599	95.25	1.339	.,.
1525	355	268	550	577	96.0	...	...
2965	1.68	12.7	551	564	97.7	..	...
3910	1.04	7.9	552	560	98.5	...	...
5565	0 61	4 6	494	499	99.0	.	1.570

[a] Percentage of free acid calculated as phthalic anhydride.

TABLE III
ISOTHERMS OF FREE ACIDITY AND PERCENTAGE OF ESTERIFICATION CHANGE WITH TIME (*T*, 220°)

Time, min.	Acid no.	Ester no.	Sap. no.	Ester, %
0	(534.5)	0	(534.5)	0
1.5	183	295	480	62
3.0	181	314	495	63.5
13.5	139	347	486	73
21.5	111	432	543	81.4
31.5	81	454	535	83
45.5	64.4	484	548	88.3
73.5	52.5	494	546	90.5
158	36.8	523	560	93.6
233	28	540	568	95
473	13.1	550	563	97.6
863	4.98	510	518	98.5
1133	3.44	602	605	99.5

TABLE IV
ISOTHERMAL DATA (*T*, 230°)

Time, min.	Acid no.	Ester no.	Sap. no.	Ester, %
0	(534.5)	0	(534.5)	0
1.5	148	252	400	63
2.5	120	286	406	70.5
6	120	328	448	73.2
12	116	342	458	74.6
19	114	385	499	77
43.5	61.4	448	509	88
57.5	55	460	515	89.4
93.5	40.6	500	541	91.5
183	24.6	525	550	96.6
303	13.6	540	554	97.6
403	8.6	530	539	98.7
553	6.6	540	547	98.9
733	3.5	535	539	99.5

TABLE V
ISOTHERMAL DATA (T, 250°)

Time, min.	Acid no.	Ester no.	Sap. no.	Ester, %
0	(534.5)	0	(534.5)	0
7	145	302	447	67.5
12	114	390	514	76.8
18	82.4	430	512	84
30	46.5	469	515	91
50	24.2	485	519	95.5
86	15.4	533	548	97.5
146	5.7	530	536	99.4
203	2.46	540	543	99.5
320	2.70	545	548	99.5
455	2.10	547	549	99.6
905	2.01	550	532	99.8
1085	1.99	535	537	99.8

III. The Effect of Temperature.—The reaction of ethylene glycol and phthalic anhydride was studied not only at 190°, but also by making runs as nearly isothermal as possible at 220, 230 and 250°; the results are given in Tables III, IV and V, respectively. The isotherms of free acidity are plotted in Fig. 1 and show that the effect of carrying out the reaction at a higher temperature is to reduce the amount of free acid more rapidly than at a lower temperature. The isotherms of the percentage of esterification given in Fig. 2 show the effect of increasing the speed of the reaction by increasing the temperature.

The resinous product of the reaction is completely volatilized at 400°.

In the case of the glycerol-phthalic anhydride reaction, it was shown[1] that plotting on semi-log paper the time to attain gelation against the reciprocal of absolute temperature resulted in a straight line. Since no gelation occurs in the ethylene glycol–phthalic anhydride reaction, it is not possible to use this transition point as a measure of a particular stage in the reaction. However, any definite percentage of esterification furnishes a suitable measure of the extent to which the reaction has taken place. Thus, taking 95% esterification, although other percentage esterifications may be taken equally well, it is possible by referring to Pig. 2 to set up a relationship between temperature and the time necessary to reach a definite percentage of esterification. The interpolated values of time necessary to produce 95% esterification at each temperature are given in Table VI.

TABLE VI

INTERPOLATED TIMES

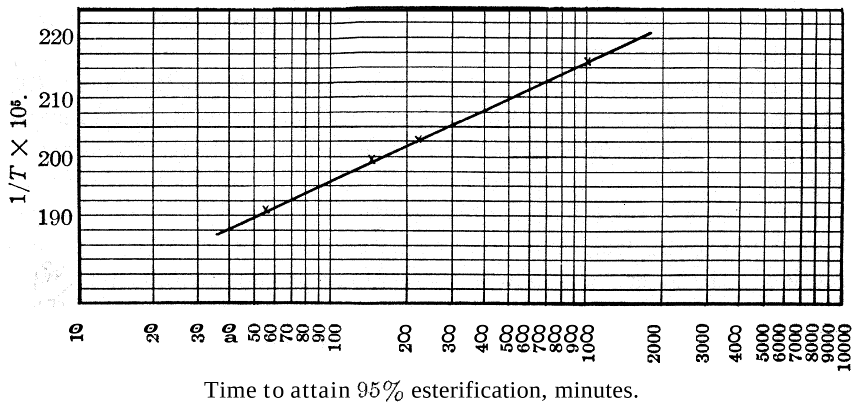
Temp., °C.	Temp., °Abs.	$1/T \times 10$	Time at which esterification = 95% (obtained from Fig. 2), min.
190	463	216	1000
220	493	203	220
230	503	199	145
250	523	191	55

Plotting these data in Fig. 4 again shows a linear relationship for the log time vs. the reciprocal of the absolute temperature.

Discussion

The data of the ethylene glycol–phthalic anhydride reaction again show that in the formation of polyhydric alcohol–polybasic acid esters, the principal reaction is that of esterification, no intermediate aldehyde formation occurring. The change in all the properties is progressive and continuous, making it plausible that the esterification takes place according to the chance meeting of the individual alcohol and acid radicals, resulting in a mixture of esters instead of the formation of simple mono- or di-esters.

The ethylene glycol–phthalic anhydride reaction differs from that of glycerol–phthalic anhydride in that the reaction can be carried practically to completion without gelation, although the kinetic data of the two reactions give similarly shaped curves. This marked change in physical properties of the resinous product by simply substituting a dihydric alcohol for a trihydric alcohol is significant in theories of resin formation. The importance of the number of reacting groups on the inter-reacting molecules is clearly shown.



Pig. 4.—Relationship of time to attain definite percentage esterification *vs.* reciprocal of absolute temperature.

Linear relationship between the reciprocal of the absolute temperature and the log of the time necessary to reach a definite percentage of esterification points out how these poly-ester reactions obey Arrhenius' equation[7] relating to the effect of temperature on chemical reactions

$$\log_e \frac{k_1}{k_2} = \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Since the reaction at each temperature has been carried to the same end-point

$$k_1 \infty \frac{1}{t_1} \text{ and } k_2 \infty \frac{1}{t_2}$$

therefore

$$\log_e \frac{t_2}{t_1} = \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Applying this equation to the data given in Table VI, it is possible to calculate the heat of activation for the reaction, the order of magnitude of which is characteristic of many chemical reactions, *viz.*, 22,600 calories.

Summary

1. The glycol–phthalic anhydride reaction is similar to the glycerol–phthalic anhydride reaction in that: (a) the reaction proceeds by esterifica-

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[7] Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Company, New York, Vol. II, p. 900,

tion, since water and resin are the only products. No intermediate aldehyde is formed. (b) The reaction, when carried on at a temperature at which both reactants are liquid, goes very rapidly at the start, evolving heat and is apparently about one-half complete within one minute of mixing. (c) As the reaction proceeds under isothermal conditions, the free acidity decreases, and the percentage esterification and the flow point increase. (d) The properties and appearance of the resinous products are similar except that the phenomenon of gelation possessed by the product of the glycerol–phthalic anhydride reaction is not possessed by the product of the ethylene glycol–phthalic anhydride reaction.

2. The glycol–phthalic anhydride reaction is dissimilar to the glycerol–phthalic anhydride reaction in that: (a) gelation of the resinous product does not take place at any temperature at which the reaction is carried out. The product remains fusible and soluble. (b) The reaction may be carried practically to completion, because gelation does not interfere with its normal course

SCHENECTADY, NEW YORK

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

SOME NEW DERIVATIVES OF DIPHENYLCARBAMINE CHLORIDE

BY THEODORE W. EVANS[1] AND WILLIAM M. DEHN

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Recently the probable –OM rather than the –NM linking in salts of cyclic imides was shown. Since the reactions of metallic sodium on aniline and acetanilide are remarkably different, it was thought that the constitution of sodium acetanilide is $C_6H_5{-}N{=}CONaCH_3$, rather than $C_6H_5{-}N{-}NaCOCH_3$. When this salt is treated with RI, etc., the R or other group is known to be linked to nitrogen; however, this linking can result from either of the two forms of the salt, from the –NNa form by direct substitution and from the –ONa form by initial addition, followed by a splitting off of sodium chloride, as indicated in the equation

$$C_6H_5N{=}CONaCH_3 + RI \longrightarrow C_6H_5NRICONaCH_3 \longrightarrow C_6H_5NRCOCH_3 + NaI$$

Since diphenylcarbamine chloride[2] reacted with many bases to yield additive compounds, it was anticipated that it would react with this salt to give some indication of addition. This was found to be the case.

When the sodium salt of acetanilide is suspended in toluene, treated with its equivalent of diphenylcarbamine chloride dissolved in toluene,

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[1] The material presented in this paper is part of a thesis submitted by Theodore W. Evans, du Pont fellow for 1929–1930, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1930.

[2] Platt and Dehn, THIS JOURNAL, 37, 2122 (1915).

and the mixture is heated gently, a clear solution is obtained.[3] Since the original salt is insoluble in toluene, this clear solution must contain a solute other than the original salt or sodium chloride, which latter is precipitated from the clear solution by boiling or by merely permitting it to stand. After filtering, etc., the acetyltriphenylurea was obtained.

Similar evidence of the formation of an intermediate additive compound was obtained with the sodium salt of acetyl-*p*-phenetidine and diphenylcarbamine chloride in toluene solution.

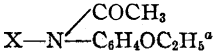
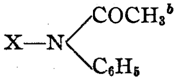
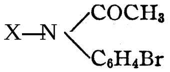
Other condensations were studied. Whereas piperidine reacts exothermically with diphenylcarbamine chloride, pyrrole could be condensed with the latter only by employing its potassium salt. The diphenylthiocarbamic esters, Ph_2NCOSR, formed from the mercaptans, constitute a new type of compound.

Experimental

The methods studied to produce condensation products were three. **(A)** Equivalents of the compound studied and diphenylcarbamine chloride

TABLE I

DERIVATIVES OF DIPHENYLCARBAMINE CHLORIDE

Compound used	Method	Formula X = Ph_2NCO-	Crystd. from	Crystal form	M. p., °C.	Nitrogen Calcd.	Nitrogen Found
Na acetyl phenetidine	C	 $X\text{—}N\begin{cases}COCH_3\\C_6H_4OC_2H_5{}^a\end{cases}$	Alcohol	Prisms	131	7.49	7.27
Na acetanilide	C	 $X\text{—}N\begin{cases}COCH_3{}^b\\C_6H_5\end{cases}$	Alcohol	Prisms	144	8.48	8.38
Na *p*-Br-acetanilide	C	 $X\text{—}N\begin{cases}COCH_3\\C_6H_4Br\end{cases}$	Alcohol	Prisms	137	6.84	6.95
K pyrrole	C	$X\text{—}NC_4H_4$	Alcohol	Needles	117	10.68	10.76
Piperidine	B	$X\text{—}NC_5H_5$	Ether	Prisms	110	10.18	9.66
Sodium	B	$(X)_2$	Toluene	Prisms	187	7.14	7.41
o-Cl-aniline	B	$X\text{—}NH\text{—}C_6H_5Cl$	Toluene	Prisms	115	8.68	8.37
m-Cl-aniline	B	$X\text{—}NH\text{—}C_6H_4Cl$	Toluene	Needles	129	8.68	8.23
p-Cl-aniline	B	$X\text{—}NH\text{—}C_6H_4Cl^c$	Toluene	Plates	169	S	S
Na ethylmercaptan	C	$X\text{—}S\text{—}C_2H_5$	Toluene	Leaflets	108	12.46	12.07
Na benzyl mercaptan	C	$X\text{—}S\text{—}CH_2\text{—}C_6H_5$	Toluene-ether	Needles	125	10.04	9.55
Na *p*-thiocresol	C	$X\text{—}S\text{—}C_6H_4CH_3$	Toluene	Plates	180–182	10.04	9.79

[a] Calcd.: C, 73.77; H, 5.92. Found: C, 74.03; H, 6.10. [b] Calcd.: C, 76.33; H, 5.49. Found: C, 76.13; H, 5.53. [c] Calcd.: Cl, 10.99. Found: Cl, 11.38.

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[3] For a somewhat similar case involving acetoacetic ester see Michael, *Ber.*, 38, 3217 (1905); this was claimed to be due to colloidal sodium chloride by Paal, *ibid.*, 39, 1436 (1906). Our case seems to be essentially different from Michael's in that the sodium chloride is much more readily precipitated, and when once precipitated it does not redissolve; also, similar solutions are not obtained with metallic salts where addition should not be expected, *e. g.*, with the sodium salts of the mercaptans.

were melted together. (B) They were boiled for several hours in toluene. (C) The sodium salt of the compound to be condensed was heated with with diphenylcarbamine chloride in toluene solution. Upon filtering and evaporation of the toluene solution, the product usually crystallized out; otherwise, ether was added and the solution cooled with ice. The products were purified by recrystallization.

Diphenyl-p-phenetylacetylurea was prepared by method (C) and also by direct acetylation of diphenyl-*p*-phenetylurea.

Summary

1. Diphenylcarbamine chloride reacts with the sodium salt of acetanilide to give first an additive compound. This indicates that the salt possesses the enol structure.

2. A number of new derivatives of diphenylcarbamine chloride have been prepared.

SEATTLE, WASHINGTON

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

ORGANIC OXIDATIONS BY IODIC ACID

BY THEODORE W. EVANS[1] AND WILLIAM M. DEHN

RECEIVED MAY 26, 1930 PUBLISHED SEPTEMBER 5, 1930

This acid has been used only rarely, exclusively in acid solutions and almost entirely for producing color effects.[2]

We have found that iodic acid can be applied in neutral solution, as, for example, its characteristic effect on amidol; in acid solutions, with most amines and phenols; in alkaline solutions, with mercaptans, thioureas and benzoin. Because it has no effect on alcohols, most alkaloids,[3] gluco-

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[1] The material presented in this paper is from part of a thesis submitted by Theodore W. Evans, du Pont fellow for **1929–1930,** in partial fulfilment of the requirements for the degree of Doctor of Philosophy, **1930.**

[2] For a voluminous bibliography on the color tests for morphine, see Merck's "Reagenzien Verzeichnis," **1924.** For Strychnine, see Selmi, *Ber.,* **11, 1692 (1902).** For emetine, Peroni, *Boll. chim. farm.,* **273 (1907).** The naphthols, Vincent, "Mcrck's Report," **1902,** p. **59.** Guaiacol, Guerine, *J. pharm. chim.,* **173 (1903).** Adrenalin, Frankel and Allers, *Biochem. Z.,* **18, 40 (1904);** Ewins, *J. Physiol.,* No. *4,* **110 (1910);** Bayer, *Biochem. Z.,* **20, 183 (1906);** Krauss, *ibid.,* **22, 131 (1908).** Since iodic acid gives color tests with creatinine and uric acid [Vitali, *L'Orosi,* 21, *73* (1898)], the following tests for components of urine by iodic acid are doubtful: glucose, Jaworowski, *Chem. Z.,* **269 (1907);** *Z. anal. chem.,* **42, 463 (1907);** bile pigments, Copranica, *ibid.,* **22, 626 (1883);** acetoacetic acid, Riegler, *Pharm.-Ztg.,* **1902, 249.** Aniline was oxidized to aniline black, Ostrogovich and Silbermann, *Bul. chim. soc. Roman stiinte, 16,* **128 (1913).**

[3] Warneke, *Arch. Pharm.,* **226, 281** (1888), oxidized wrightine to oxywrightine by iodic acid; this product by means of other oxidizing agents has been attempted in vain.

sides, carbohydrates, etc., it is concluded that it is very selective in its action. Symmetrical diaryl thioureas give the corresponding ureas, but asymmetrical diaryl thioureas, all tri- and tetra-substituted thioureas are without action, as also are the mustard oils, and disulfides, sulfoxides, etc.

Through the use of iodic acid we have been able to develop improved methods of preparation of the disulfides, aryl cyanamides, symmetrical diaryl ureas, purpurogallin and benzilic acid.

Experimental

A large number of amino and phenolic compounds, alkaloids and glucosides were tested for the oxidizing effect of iodic acid. The method employed was to place in a beaker some aqueous iodate solution, a few milligrams of the substance to be tested, a few drops of acetic acid and pieces of silk and cotton cloth. The mixture was boiled until the dye was fixed on the fabrics. With the different amino and phenolic compounds every imaginable shade of brown was obtained on the silk. In most cases no dye was fixed on the cotton; whenever fixed, light browns, buffs and ochers were obtained. The diamine and alkylated anilines, especially, gave beautiful shades of brown. Some of these amino and phenolic compounds will be investigated.

Color Tests on Silk.—Phenol, light brown; catechol, guaiacol, resorcinol, diresorcinol, deep brown. The naphthols, yellow-brown, eugenol, gold-brown. Quinol, brown. Procaine, butyn, anesthesine, *p*-aminobenzoic acid, light brown. Aminophenol and amidol, red-brown; *p*-aminophenol, dark brown. Phloroglucinol, blood-red. After hydrolysis with hydrochloric acid, phoridzin, through yellow to blood red. This is the only glucoside that gave a positive test. Apomorphine, beautiful light green, through chrome green to green-black on silk; greenish-gray on cotton. Boldine and apocodeine, brown.

Action on Mercaptans.—A mixture of 3 g. of *p*-thiocresol, 6 g. of sodium iodate, 6 g. of sodium hydroxide and 90 cc. of water was heated on the water-bath for an hour. When cooled and neutralized, the di-p-tolyldisulfide precipitated. After recrystallization from alcohol it melted at 46°.

In an analogous manner dibenzyldisulfide, melting at 71°, was prepared.

Action on Thioureas.—Equal weights of thiocarbanilide, sodium iodate and sodium hydroxide in 100 cc. of water were heated to boiling until a plastic mass in the water was obtained. If this is filtered hot and washed with water, pure diphenylurea is obtained.

In a similar manner, 3,3'-dinitrothiocarbanilide yielded 3,3'-dinitrodiphenylurea, melting at 233°; phenyl-*p*-tolylthiourea gave phenyl-p-tolylurea melting at 212".

Ethyl-N,N'-diphenylthiourea, N,N-methylphenylthiourea and N,N'-diphenylbenzylthiourea failed to react with iodate.

Preparation of Aryl Cyanamides.—When a mixture of equal weights of phenylthiourea, sodium iodate, sodium hydroxide and a double mass of water was heated to boiling for ten minutes, then cooled, filtered[3] and neutralized with acetic acid, a plastic

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[3] In the preparation of these aryl cyanamides, small quantities of the corresponding diarylureas always were formed—these constitute the precipitates found at this point.

mass precipitated. After decanting, washing with water and letting stand, it solidified. Its identity was established by heating with aniline, thus forming diphenylguanidine, melting at 147°.

In a similar manner o-tolylcyanamide and *p*-tolylcyanamide were prepared.

The Preparation of Purpurogallin.—When 100 cc. of a cold aqueous solution containing 8 g. of sodium iodate is slowly added with constant stirring to 10 g. of pyrogallol[4] dissolved in a little cold water, the reaction proceeds smoothly with a precipitation of 7.6 g. of purpurogallin. Assuming the reaction to be

$$2C_6H_6O_3 + NaIO_3 = C_{11}H_8O_5 + CO_2 + NaI + H_2O$$

this is equivalent to a 92% yield.

In order to test the validity of this equation, the carbon dioxide evolved was determined by absorbing it in a potash bulb. In two determinations each starting with 10 g. of pyrogallol and 8 g. of iodate, 1.2902 and 1.2899 g. of carbon dioxide were obtained. In each case the yield of purpurogallin was 6.5 g. These figures represent a 78% yield of purpurogallin and a 74% yield of carbon dioxide. This would seem to indicate that for each molecule of purpurogallin formed a corresponding molecule of carbon dioxide is liberated.

The Preparation of Benzilic Acid.—Benzoin is directly convertible into benzilic acid by the action of sodium iodate in concentrated sodium hydroxide. When it is added to a hot concentrated solution of these, the reaction proceeds spontaneously, and substantially a quantitative yield of benzilic acid is obtained, in accordance with the reaction

$$3C_6H_5CHOHCOC_6H_5 + NaIO_3 + 3NaOH = 3(C_6H_5)_2COHCOONa + 3H_2O + NaI$$

From Pure Benzoin.—To a beaker containing 20 g. of sodium hydroxide and 7 g. of sodium iodate, sufficient water is added to make a boiling hot solution; then 20 g. of benzoin is put in and stirred with a rod. The purplish colored mixture is then heated and stirred. Finally, when the purple color is entirely discharged, sufficient water is added to dissolve the solids to a clear solution. Concentrated hydrochloric acid is gradually added and the iodine and traces of benzoic acid are expelled by boiling. On cooling, filtering and drying, about 20 g. of crude benzilic acid is obtained. This is dissolved in boiling benzene, filtered and cooled rapidly, when about 18 g. of pure benzilic acid is obtained. From the benzene filtrate 2 g. of impure benzilic acid may be recovered. The crude benzoin obtained from benzaldehyde may be used directly in this preparation, but a lessened yield is obtained.

Summary

Iodic acid has been shown to be a very selective oxidant. By its use various improved preparations have been developed.

SEATTLE, WASHINGTON

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[4] Various oxidizing reagents have been used to prepare purpurogallin from pyrogallol. These were compared by Perkin and Stevens, who contributed what they considered the best reagent, namely sodium nitrite and acetic acid. Their best yields were 30–40% [*J. Chem. Soc.*, 83,194 (1903)].

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE MOLECULAR WEIGHT OF LACTALBUMIN

BY BERTIL SJÖGREN AND THE SVEDBERG

RECEIVED MAY 27, 1930 PUBLISHED SEPTEMBER 6, 1930

A first attempt to study the dispersity of the proteins of milk by means of ultracentrifugal methods was made by Fåhraeus and one of the present writers in 1924.[1] Cows' milk was submitted to the action of a centrifugal field about 1500 times the force of gravity and exposures were taken at intervals of one hour. From the rate of sedimentation and the spreading of the boundary it was concluded that the natural casein—or calcium casein compound—of milk is a polydisperse colloid of comparatively low degree of dispersity, containing particles of radius ranging from about 10 to 70$\mu\mu$. The behavior of purified casein in centrifugal fields up to 100,000 times the force of gravity was studied by Carpenter.[2] The latter investigation showed that casein is a very unstable protein and that the molecular weight and degree of homogeneity of the product depend on the method of preparation which has been used. The sedimentation constant for casein isolated by the method of Van Slyke indicates a molecular weight around 100,000 for the bulk of this protein material—a value which is in the neighborhood of the molecular weight of serum globulin. Heating to 40° for one hour caused an increase in molecular weight to about double, and treatment with acidified 70% alcohol at 40° after the manner of Linderström-Lang gave a product which possessed a molecular weight nearly four times that of the original casein.

Besides the casein the chief protein constituent of cows' milk is the lactalbumin. It occurs to about 10% of the amount of casein. In view of the complicated behavior of casein it was thought to be of interest to collect some data concerning the dispersity of lactalbumin in order to see whether the very marked instability observed for casein also occurs in the lactalbumin and, therefore, is to be considered as a characteristic of the milk proteins.

Preparation of Lactalbumin.—Seven thousand cc. of fresh cows' milk of P_H 6.7 and containing some toluene was run through a separator to remove the fat. Saturated ammonium sulfate solution was added to 50% saturation and the P_H of the mixture brought to 5.2 by means of acetic acid. After standing for twenty-four hours in the ice box the precipitate of casein and globulin was centrifuged off and saturated ammonium sulfate solution added to 80% saturation. After twenty-four hours in the ice box the albumin precipitate was centrifuged off and washed with a weak solution of ammonium sulfate. The precipitate was dissolved in water and brought to crystalliza-

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[1] T. Svedberg, *Kolloid-Z.*, 51, 10 (1930).

[2] T. Svedberg, L. M. Carpenter and D. C. Carpenter, THIS JOURNAL, 52, 241, 701 (1930).

tion at room temperature by the addition of ammonium sulfate and sulfuric acid.[3] The crystals were dissolved in water, dialyzed against toluene-saturated water at 5° until the sulfate reaction was negative and finally electrodialyzed with a current density of 0.6 milliampere per sq. cm. for thirty hours. No precipitation occurred during the electrodialysis; volume of solution 175 cc.; concentration 0.74% (Material I).

Another sample of lactalbumin was made up from an equal quantity of milk proceeding as described above but omitting the crystallization process. The volume of the final solution was 200 cc. and the concentration 3.14% (Material II).

Specific Volume, Isoelectric Point and Light Absorption of Lactalbumin.—The partial specific volume was measured pycnometrically at 20°. Material II was used and determinations were carried out in electrolyte-free solutions at 3.14 and 2.04%. The values agreed within experimental error and gave V = 0.750.

The isoelectric point of Material II was determined by means of the photographic cataphoresis method worked out in this Laboratory by A. Tiselius.[4] The protein was found to be electrochemically inhomogeneous and to possess an isoelectric point of approximately Pa 5.2.

The light absorption was measured on Material II by means of the Judd-Lewis spectrophotometer. The solution was electrolyte-free, of concentration 0.1% and thickness of layer of 2.0 cm. The specific extinction coefficient $\epsilon/c = 1/cd \times \log I_0/I$ (where c is the concentration, d the thickness of the solution, I_0 the intensity of the light beam after passing through the solvent and I the intensity after passing through the same thickness of solution) had a maximum value of 10.6 at a wave length of 279μμ and a minimum value of 3.6 at 255μμ. In Fig. 1 the absorption curve is given.

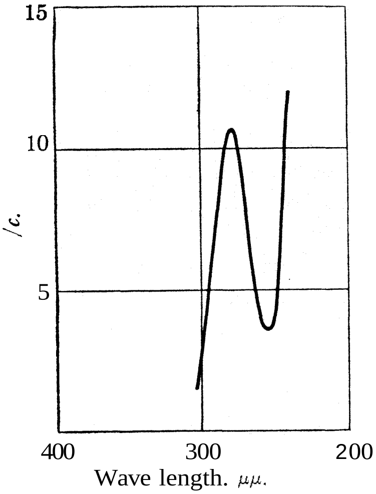

Fig. 1.

Molecular Weight and Sedimentation Constant of Lactalbumin.—A sedimentation equilibrium measurement was carried out on the crystallized Material I at a speed of 11,200 r. p. m. The protein concentration was 0.10% at the start and the solution 0.025 M in KH_2PO_4 and 0.025 M in Na_2HPO_4, giving a PH of 6.8. The molecular weight was calculated from the relation

$$M = \frac{2\,RT\ln\,(c_2/c_1)}{(1 - V\rho)\,\omega^2(x_2^2 - x_1^2)}$$

where R is the gas constant, T the absolute temperature, V the partial specific volume of the solute, p the density of the solvent, *w* the angular velocity and c_2 and c_1 are the concentrations at the distances x_2 and x_1 from the center of rotation.

The values of the molecular weight were not independent of the distance

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[3] A. Wichmann, *Z. physiol. Chem.*, *27*, 575 (1899).

[4] A. Tiselius, "Dissertation," Upsala, 1930.

from the center of rotation but varied from 12,000 at a distance of 5.50 cm. to 25,000 at a distance of 5.90 cm.

In Table I are given the results of two sedimentation velocity runs made on Materials I and II.

TABLE I

LACTALBUMIN SEDIMENTATION VELOCITY RUNS

Material	Solvent		*Pa* of	Concn. of		Remarks
	KH_2PO_4, M	Na_2HPO_4, M	soln.	protein, %	$S_{20°} \times 10^{13}$	
I	0.019	0.001	5.5	0.27	2.22	a
II	.025	.025	6.8	.63	2.95	b

[a] Strong drift in diffusion constant; trace of non-centrifugible material.

[b] Drift in diffusion constant; no non-centrifugible material.

Material II was again tested after having been left for three months in the ice box. The sedimentation constant was approximately the same but about 15% of the protein was broken up into a non-centrifugible substance.

The drift in the values of the molecular weight with distance from the center of rotation as well as the drift observed in the apparent diffusion constant shows that lactalbumin is not homogeneous with regard to molecular weight. In this respect therefore it resembles casein.

Direct Ultracentrifugal Analysis of Milk and of Lactalbumin at Different Stages of Purification.—The fact brought out by the above measurements that lactalbumin is not homogeneous with regard to molecular weight made it desirable to study the dispersity of this protein at different stages during the process of purification in order to ascertain whether the inhomogeneity is caused by the procedure of isolation.

Sedimentation velocity runs at high speed (centrifugal force about 100,000 times the force of gravity) during three to four hours at a temperature of 20–23° were used for testing the material.

Fresh milk (PH 6.8) was first centrifuged without any treatment at all. At the high speed used the casein is thrown down in a few minutes. After that period only a very slight sedimentation occurred (Fig. 2A, time between exposures, one hour). The bulk of the light-absorbing material (65–80%) was non-centrifugible. Addition of acetic acid until a molarity of 0.02 was reached with a PH of 5.8 had no effect on the sedimentation. The PH of the milk was then raised to 10.3 by the addition of sodium hydroxide until the molarity was 0.02. The sedimentation remained the same. Dilution of the milk with water or with a 2% solution of ammonium sulfate to two-ninths of the original concentration slightly increased the sedimentation.

In order to eliminate the influence of viscosity caused by the presence of the lactose, a sample of milk containing toluene was dialyzed against water for three days in the ice box. Only a slight increase in sedimentation occurred. Addition of 5% ammonium sulfate to the dialyzed milk had no effect.

These experiments show that untreated milk and milk the P_H of which has been lowered to 5.8 or raised to 10.3 and milk treated with ammoniuni sulfate up to 5%, or milk which has been freed from lactose and salts by dialysis contain but a small quantity of lactalbumin of the degree of dispersity observed in the product isolated by the usual method. In the milk the lactalbumin is present in a very much higher degree of dispersity than in the finished laboratory product.

A lowering of the P_H of the milk to 4.1 either by the addition of hydrochloric acid or acetic acid raised the sedimentation constant slightly above 2×10^{-13} and converted part of the non-centrifugible material into centrifugible substance.

A sample of milk was half saturated with ammonium sulfate, the casein–globulin precipitate removed and the solution dialyzed against water in the ice box for two days. The sedimentation constant was identical with that for lactalbumin as determined above. The non-centrifugible material had decreased considerably and now only amounted to about 20% (Fig. 2 B, time between exposures one-half hour).

A similar experiment was performed with milk from which the casein had been removed by precipitation with acetic acid. The product showed the same properties as the one just described.

To another sample of milk was added ammonium sulfate to saturation. After standing for twenty-four hours in the ice box the precipitate was dialyzed against water until the sulfate reaction was negative (five days). The casein–globulin precipitate was removed and the solution tested in the ultracentrifuge; the sedimentation constant and amount of non-centrifugible material were as before.

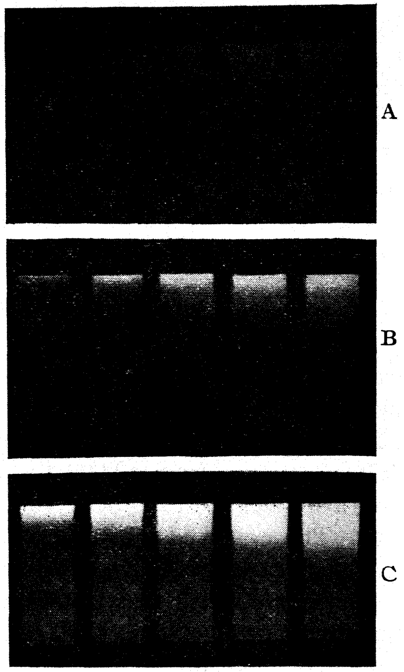

Fig. 2.

The treatment to which the milk was subjected in the last three experiments is identical with the chief processes of isolation used for the preparation of lactalbumin. As a matter of fact this treatment brought about a considerable change in the properties of the original albumin of the milk toward the properties found in the "purified" lactalbumin. The sedimentation constant was practically the same but the material still contained about 20% of non-centrifugible substance.

For the sake of comparison a picture of the sedimentation of the purified lactalbumin (Material II) is given in Fig. 2 C (time between exposures forty min.).

From the above experiments it is obvious that the lactalbumin is an artificial product built up during the process of "purification" from some material of low molecular weight present in the milk. The degree of dispersity or molecular weight of this non-centrifugible material we have not as yet made any attempt to determine. We have ascertained that it is almost completely precipitated by saturation with ammonium sulfate and that it does not diffuse through collodion bags. From the centrifuging tests it follows that the molecular weight cannot be higher than about 1000. The molecular weight of the "purified" lactalbumin was found to range from 12,000 to 25,000, which shows that the molecular weight of the original lactalbumin of the milk has been raised many times in the "purification" process.

The expenses connected with these experiments have been defrayed by a grant from the foundation "Therese och Johan Anderssons Minne."

Summary

1. The molecular weight and sedimentation constant of lactalbumin prepared from cows' milk were determined by means of the ultracentrifugal methods.

2. Lactalbumin is not homogeneous with regard to molecular weight. Values ranging from 12,000 to 25,000 were observed. The mean sedimentation constant lies between 2 and 3 times 10^{-13}.

3. The observed inhomogeneity of lactalbumin suggested ultracentrifugal tests at different stages during the process of purification.

4. It was found that lactalbumin with the properties observed in the "purified" product does not exist in the milk, but is formed during the process of "purification," especially by the action of ammonium sulfate of high concentration.

5. The bulk of the material from which the lactalbumin is formed has a low molecular weight not exceeding 1000. The comparatively high molecular weight of the final product is a result of gradual aggregation of the material of low molecular weight originally present in the milk.

6. The pronounced instability of casein with regard to molecular weight as found by Carpenter also occurs in lactalbumin and this property is, therefore, probably a characteristic of the milk proteins and may be of considerable physiological importance in nutrition.

UPSALA, SWEDEN

[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

REDUCTION REACTIONS WITH CALCIUM HYDRIDE. II. DETERMINATION OF SULFUR IN SULFUR OILS AND RUBBER[1]

BY WILLIAM E. CALDWELL WITH FRANCIS C. KRAUSKOPF

RECEIVED MAY 31, 1930 PUBLISHED SEPTEMBER 5, 1930

Oxidative methods used at present for the determination of sulfur in sulfur-containing oils and rubber are time-consuming and painstaking. Having obtained satisfactory results by the reductive method for determining the sulfur content of sulfates, using a preliminary heating with calcium hydride, it seemed desirable to apply this method to the sulfur analysis of other substances.

When volatile sulfur-containing compounds are to be dealt with, as in rubbers or oils, we would no longer be able to carry on open heatings with calcium hydride as in a sulfate analysis. The volatile sulfur-containing compound must be mixed with the powdered hydride in a bomb and the whole heated to around 750°. The residue from such heatings should contain all the sulfur as calcium sulfide, which as a water-soluble sulfide may be iodimetrically determined.

Materials.—In order to test this new method as to its applicability in sulfur determinations on oils and rubbers, many samples of varying sulfur content were obtained. Definite sulfur percentages on these oils as determined by oxidative and reductive methods are given in Table I. Eight sulfur-bearing oils, used in industry as cutting and lubricating oils, were analyzed.

Ten different rubber samples obtained from rubber companies were also ground to a finely divided state, sampled and analyzed. The variance in the nature of these rubber samples, with results of analyses upon them, are to be noted in Table II.

It was found difficult to prepare finely divided samples of these rubbers such that an intimate mixture could be made with the powdered hydride. Some of the rubbers could be cut into shreds with scissors and then into small cubes. This is laborious and one still does not have the rubber finely divided. The best method was to use an emery wheel, which quite readily ground the rubber into a finely divided condition. This was especially true of the hard and semi-hard rubbers, and on grinding them a suitable powder was obtained which with calcium hydride gives an intimate mixture. The softer rubbers and gums on being ground would yield

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[1] This paper is prepared from the latter part of a dissertation on reduction reactions with calcium hydride, presented by William E. Caldwell in partial fulfilment of the requirements for the degree of Ph.D. The first part was published in THIS JOURNAL, 51,2936 (1929).

particles which would again agglomerate. An intimate heating mixture was impossible in their case and our later results show that we had a correspondingly low result in sulfur percentage due to incomplete action with the calcium hydride.

Bombs.—Small bombs of about three-fourths of a cubic inch capacity were used. In the course of the work bombs of different design were used in endeavoring to hold all the gas formed within the bomb. The requirements for a bomb for this work are quite stringent. Because the mass within must be heated to about 800°, the bomb must withstand that temperature and a copper gasket must be used. An attempt was made to estimate the pressure that would be reached in the bombs.

Assuming that a 1-g. sample of an oil with an average molecular weight of 224 is taken, and that the gas capacity of the one-half filled bomb is about 10 cc.

224 g. of oil would yield 22,400 cc. of gas at 0° and 760 mm.

1 g. of oil would yield 100 cc. of gas at 0° and 760 mm.

P, 1 atm.; V, 10 cc. air + 100 cc. (potential volume of oil vapor); T, 273°K.; P', x; V', 10 cc.; T', 1073°K.

$$\frac{PV}{T} = \frac{P'V'}{T'}$$

$$P' = 43.2 \text{ atm.}$$

$$43.2 \times 14.7 = 625 \text{ pounds per sq. inch}$$

Considering these assumptions, a pressure of six hundred and twenty-five pounds per square inch may be built up in the bomb. The pressure could be more if cracking of the oil to smaller molecules occurred or if an oil of a smaller average molecular weight were taken. Pressure might also be developed by decomposition of the hydride to calcium and hydrogen vapors. However, the pressure may be considerably less in that much calcium carbide is formed and organic matter thus combined in the solid state.

Accordingly a bomb must be made of materials of such thickness as to withstand these pressures and temperatures. On the other hand, a bomb of as little weight as possible is desired so that heating and cooling may be rapid.

It is admitted that we have not developed a wholly satisfactory bomb for use in this work. Bombs have allowed gas to leak by the gaskets and through the threads. This is considered then to be the source of low results in the determination of sulfur in very volatile oils containing low molecular weight mercaptans, disulfides, etc.

Solutions and Calcium Hydride.—Carefully standardized 0.1 N iodine and sodium thiosulfate solutions were used as in previous work for determining the water-soluble sulfide in the residue after the heating of sulfate compounds with hydride. A calcium hydride powder of less than sixty mesh was used in intimate contact with the oil and rubber in a manner similar to that in the work on insoluble sulfates.

Experimental

Sulfur Content of Oils. —Weighed amounts of the oils are poured into the bombs containing about 7 g. of the powdered calcium hydride. The oil is quite readily mixed with the hydride by means of a small glass rod. A gram or two more of the hydride is pressed into the bomb over the oil–powder mixture. The bomb is tightly sealed and quickly heated to redness in a muffle furnace or over a Méker burner. After the bomb has been at a bright red heat for ten minutes it is allowed to cool. The contents are readily removed from the bomb and placed in a 500-cc. Erlenmeyer flask. The residue is moistened with about 20 cc. of dry alcohol. This is to prevent dusting, which would occur if water were immediately dropped upon the hydride. Water is now slowly added to the moistened fusion mass from a dropping funnel which is above a reflux condenser at the bottom of which is placed the Erlenmeyer flask. After the excess hydride and the carbide formed have been decomposed, additional water is added to make a solution of about 400 cc. It is well to add some ice in place of a portion of the water so that the solutions will be cool for a better end-point in ensuing titrations.

Before iodine titration, the mass is placed in a liter beaker and an excess of concentrated hydrochloric acid added with a minimum of stirring. The large volume of water is necessary to dissolve and hold the hydrogen sulfide obtained on acidifying the calcium sulfide solution.

The resulting hydrogen sulfide solution is titrated for sulfur content with the 0.1 N iodine solution, one cubic centimeter of the iodine solution being equal to 0.0016 g. of sulfur.

Sulfur **Content** of Rubber.—Rubber samples are treated in a manner similar to that for oils except that the powdered rubber is intimately stirred into the finely divided hydride.

Sample weights of the oils and rubbers are taken so that one can expect a 10–50 cc. iodine titration. For substances expected to contain less than 3% sulfur, a sample up to 1.5 g. is taken. For a hard rubber of around 20% sulfur, a 0.25-g. sample should suffice.

Table I gives the results of sulfur analysis on oils by Eschka's oxidative method compared with percentage sulfur as determined by the above outlined reductive method. Samples 1–8 are on cutting and lubricating oils, the sulfur having been incorporated into these products by heat and pressure. The sulfur compounds so formed are not volatile at low temperature.

Three samples of petroleum oil were analyzed both by Eschka's and our methods. Neither method gave check results or indicated the total sulfur in these oils. Such an oil of low sulfur percentage and containing very volatile sulfur compounds must be treated by some digestion and oxidative method.

Table II lists results of sulfur analyses on rubbers by oxidative and reductive methods. Some other rubbers were tried with discouraging results. These rubbers were mainly of a sticky nature such that an intimate mixture of their macerated form could not be made with the powdered calcium hydride.

TABLE I

SULFUR CONTENT OF OILS

Oil no.	S content (Eschka's method), %	S content (CaH_2 method), %	Remarks
1	6.77 6.76	6.80	High sulfur oil. Used 0.7-g. sample. Heavy viscous oil
	7.08 6.55	6.91	
2	2.32	2.46 2.49	Heavy black oil
	2.46	2.50 2.25	
3	4.83	4.63 4.61 4.40	Heavy black oil
	4.79	4.54 4.62 4.63	
		4.82 4.53	
4	1.70	1.78	Animal or vegetable oil. Contains H_2O
	1.74	1.73	
5	0.275	0.33	Light oil, some oleic acid, water, little S
	0.27	0.40	
6	1.97	2.10	Light, somewhat volatile oil
	2.03	2.11	
	2.02		
7	1.4	1.46	A solid, fatty substance
	1.31	1.45	
8	3.77	4.00	Oil not wholly homogeneous. Heavy black oil
	4.00	4.25	
	3.20	3.87	

TABLE II

SULFUR CONTENT OF RUBBERS

Sample no.	Sulfur (oxidative), %	Sulfur (CaH_2 method), %	Remarks
1	22.61	21.40	A very hard black rubber. Powders readily on grinding
	22.50	22.40	
2	1.77	1.9	Soft, but grinds to fluffy powder
3	1.35	1.44	Brown shoe sole
4	1.83	1 83	Black crumbly rubber
5	1.29	1.25	Pink crumbly rubber
6	2.15	2.19	A piece of tire. Hard to macerate
7	2.76	2.63 2.51	Shoe sole or belting
8	2.75	2.68	Black rubber plate
9	1.63 1.58	1.58	Rubber casting
10	29 6	29.3 29.8	Ground fountain pen casing

Miscellaneous Sulfur Determinations.—Two 0.05-g. samples of free sulfur were heated in bombs with 5 g. of calcium hydride. The cooled residue on analysis for water-soluble sulfide gave results corresponding to 0.0512 and 0.0496 g. of sulfur. Thus free sulfur may be determined within a 2% error even on such small samples.

Samples of sodium thiosulfate were similarly treated to determine their sulfur content. Considering the sample to be $Na_2S_2O_3 \cdot 5H_2O$ it would contain 25.8% of sulfur. An average of our analyses showed it to contain 25.34%.

Discussion of Results

It is evident from a consideration of results obtained that the method here presented of determining sulfur in insoluble sulfates may be extended to the determination of sulfur in oils and rubbers when one uses a gas-tight bomb instead of the open crucible. All of the sulfur in the organic material is converted to calcium sulfide when heated to 700° in contact with calcium hydride. The water-soluble sulfide thus formed may be determined by iodimetry. The method lends itself most readily to determinations in rubbers and oils of high sulfur content, and presents itself as a rapid method for the determination of sulfur in this type of material.

Summary

1. Sulfur may be determined in sulfurated oils by fusion of the oils with calcium hydride, followed by an iodine titration on an acidified solution of the fusion residue.
2. A method of determining the percentage of sulfur in some rubbers is presented.
3. By this method it is possible to determine the percentage of sulfur in free sulfur, sodium thiosulfate and similar sulfur-containing compounds.

MADISON, WISCONSIN

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COMPOSITION OF THE GUM PRODUCED BY ROOT NODULE BACTERIA

BY E. W. HOPKINS, W. H. PETERSON AND E. B. FRED

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One of the most striking characteristics of the root nodule bacteria is the gummy or viscous nature of the colonies or streak cultures. The mucinous appearance of the cultures has been reported by many investigators[1] and has been attributed to the formation of dense capsules by the organisms. What function the gum performs in the metabolism of the bacteria or in their relation to the host plant is not known. Grieg-Smith[2] suggests that the gum is used by the plant and built into nitrogenous compounds, while Mazé[3] is of the opinion that the gum itself is the nitrogenous compound supplied the plant by the bacteria. That the latter assumption is

[1] (a) M. W. Beijerinck, *Bot. Ztg.*, 46, 754 (1888); (b) G. F. Atkinson, *Bot. Gaz.*, 18, 157 (1893); (c) L. Hiltner, *Centr. Bakt.*, II Abt., 6, 273 (1900); (d) M. Dawson, Phil. *Trans. Roy. Soc.*, B193, 51 (1900).

[2] R. Grieg-Smith, *Centr. Bakt.*, II Abt., 30, 552 (1911).

[3] M. Mazé, *Ann. de l' Inst. Pasteur*, 12, 1 (1898).

incorrect was shown by Buchanan[4] and Fred,[5] who found that the purified gum contained no nitrogen.

The properties and composition of the gum have not been thoroughly investigated. Much of the work has been of a qualitative nature, and in no case have the hydrolysis products been conclusively identified.

The nitrogen-free gums of clover[6] and of bean[4] root nodule bacteria were found to give on hydrolysis reducing sugar which was assumed to be glucose. According to Beijerinck,[7] the slime producing strains of B. *radicicola* form a "cellulan" a type of gum which, contrasted with the dextrans and levulans, is not fermentable by *Granulobacter saccharobutyricum*. Grieg-Smith[8] prepared gum from cultures of lupine and pea nodule bacteria which had specific rotations of +29.7 and 31.7°, respectively. These gums contained small amounts of nitrogen and on hydrolysis gave a sugar which from its reducing power and optical rotation appeared to be almost entirely glucose. A phenylosazone, separated into two fractions with melting points 205 and 193°, thus similar to those of glucose and galactose, was reported, but the author gives no information as to how these were obtained or analyses of their composition. Owing to the lack of particulars, it is impossible to decide whether the author had an osazone of galactose or merely a slightly impure glucosazone. It is well known that a slight impurity markedly lowers the melting point of an osazone. In a later paper by the same author,[2] the gum of bean root nodule bacteria was reported as consisting of glucose and galactose, and the specific rotation of the gums of bean, pea and lupine root nodule bacteria is given as +29°. Kramár[9] hydroyzed B. *radicicola* gum, and prepared a phenylosazone which was apparently glucosazone. Its melting point was 205°. As far as present knowledge goes, the gum of the root nodule bacteria presumably contains glucose, but there has as yet been no conclusive proof of the presence of this sugar. As to the question of the existence of galactose as a constituent of the gum, the evidence is much less convincing than that for glucose. In our own work the gum has been found on hydrolysis to give glucose and a uronic acid, but no fructose, mannose, galactose or pentoses have been found among the hydrolysis products.

Experimental

Preparation of Samples.—The gums studied in this work were produced from cultures of root nodule bacteria of three different cross-inoculation groups. The strains used were *Rhizobium meliloti* 100 (alfalfa), three

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[4] R. E. Buchanan, *Centr. Bakt.*, II Abt., 22, 371 (1908).

[5] E. B. Fred, *Virginia Agr. Expt. Sta. Report*, 145 (1911–1912).

[6] G. E. Gage, *Centr. Bakt.*, II Abt., 27, 7 (1910).

[7] M. W. Beijerinck, Fol. *Microbiol.*, 1, 377 (1912).

[8] R. Grieg-Smith, *Proc. Linn. Soc. of New South Wales*, 31, 264 (1906).

[9] E. Kramár, Centr. Bakt., I Abt., 87,401 (1921).

batches, preparations 1, 2 and 3; *Rhizobium trifolii* 205 (clover), three batches, preparations 4, 5 and 6; *Rhizobium trifolii* 201 (clover), one batch, preparation 7; *Rhizobium leguminosarum* 311 (pea), two batches, preparations 8 and 9. The media used in the preparation of these samples and the yields of gum in grams per liter are given in Table I.

TABLE I

THE COMPOSITION OF THE CULTURE MEDIA USED IN THE DIFFERENT BATCHES

	Alfalfa Preparation, g./liter			Red clover Preparation, g./liter				Pea Preparation, g./liter	
Compounds	1	2	3	4	5	6	7	8	9
Sucrose	...	10.0	10.0	...	...	...	...	...	...
Mannitol	10.0	...	...	10.0	10.0	10.0	6.0	10.0	6.0
Peptone	...	0.5	0.5	...	...	...	...	...	...
KNO_3	...	...	...	0.2	0.2	0.2	...	0.2	...
$NaNO_3$	...	...	...	...	...	...	0.05	...	0.05
NaCl	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.1
$MgSO_4$	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.1
K_2HPO_4	0.4	2.0	2.0	0.5	0.5	0.5	0.4	0.5	0.4
$CaCO_3$	0.4	...	...	1.0	3.0	...	...	...	...
$CaSO_4$	...	...	...	0.1	0.1	0.1	0.1	0.1	0.1
Yeast water, 10%	5 cc.	...	...	...	...	...	...	...	...
Agar	16.0	...	...	...	20.00	20.0	15.0	...	13.0
Yields of gum (dry weight), g. per liter	0.686	0.481	0.706	0.530	0.665	1.052	0.295	1.019	0.290

The general procedure for preparing the samples was first to test the purity of the cultures at the end of fermentation by inoculating sterile litmus milk and potato slants. All contaminated cultures were discarded. In the case of the agar cultures, the surface growth was washed from the agar and filtered through a thick layer of absorbent cotton to remove any pieces of agar. The liquid cultures were so viscous that dilution was usually desirable. The gum solution and bacterial suspension was then run through a Sharples supercentrifuge rotating at a speed of about 42,000 r. p. m. This treatment removed most of the bacteria from suspension, while the gum remained dissolved in the liquid. Concentration of the gum solution was effected in a vacuum pan at 60° and the gum precipitated by adding two volumes of acetone. This precipitate was redissolved in warm water and again precipitated, and a second resolution and precipitation conducted in the same manner for further purification of the gum. The stringy coagulum, when dried, gave a grayish-yellow cake, which was ground to an impalpable powder and dried to constant weight.

It was observed that when calcium carbonate was used in the medium, the gum precipitated as a stringy mass, while in the other media, it came down as flocculent particles. Better precipitation of the gum was found to take place in all cases when calcium chloride was added to the gum solution. This procedure was then followed to insure a maximum yield of the gum. This improved precipitation may be due to a chemical union of calcium with the gum—later work showed that the gum molecule contains a sugar acid.

Analytical Methods.—The ash was determined by ignition of 50-mg. samples. *Uronic acid anhydride* determinations were made by the procedure of Dickson, Otterson and Link.[10] The term "uronic" acid is here applied to glucuronic and galacturonic acids. Decarboxylation of the uronic acids is effected by means of hydrochloric acid and the carbon dioxide driven off estimated by absorption in alkali. For *pentosan* determinations, the Youngburg[11] micro-method of distillation with phosphoric acid was used. *Sugars* were determined by the micro-method of Stiles, Peterson and Fred.[12]

Composition of Gum.—In Table II are given the analytical results. The ash content of the samples is not consistent. Gum from agar cultures contained less ash than that from liquid cultures inasmuch as the separation from the salts of the medium was more easily accomplished in the former cases.

TABLE II

ANALYTICAL DATA ON THE DRY GUM PRODUCED BY THE ROOT NODULE BACTERIA

Prepn.[a]	Sample	Ash, %	Uronic acid anhydride, ash-free basis. %	Pentosans (apparent) furfural X 1.71 (ash-free), %	Pentosans (actual)[b] (ash-free), %	Reducing sugar as glucose (ash-free basis), %
1	Rhizobium meliloti 100 a	6.1	4.1	7.5	6.2	72.8
2	Rhizobium meliloti 100 b	52.8	6.8	4.3	2.2	
3	Rhizobium meliloti 100 c	26.2	4.5	5.9	4.5	
4	Rhizobium trifolii 205 a	15.5	22.1	11.3	4.5	
5	Rhizobium trifolii 205 b	9.6	24.8	16.4	8.6	
6	Rhizobium trifolii 205 c	7.9	22.3	16.1	9.2	75.267.3
7	Rhizobium trifolii 201	9.2	25.3	10 5	2.7	82.2 75.6
8	Rhizobium leguminosarum 311 a	21.6	19.3	10.3	3.9	61.2 52.8
9	Rhizobium leguminosarum 311 b	10.8	22.0	12.6	5.8	

[a] In Sample 1, calcium carbonate in medium but no calcium chloride was added to the gum solution. In Samples 2 and 3, no calcium carbonate in medium and no calcium chloride was added to the gum solution. In Samples 4 and 5, calcium carbonate was present in the medium and calcium chloride was added to the gum solution. In Samples 6, 7, 8 and 9, no calcium carbonate in medium, but calcium chloride was added to the gum solution. [b] (Total furfural – furfural from uronic acid) X 1.71.

The uronic acid content of the gums shows great variation. Pea and red clover nodule bacteria gums contain between 19.3 and 25% of the acid anhydride, while the gum of alfalfa nodule bacteria contains only about one-fourth as much anhydride.

In the calculations of the pentosan figures given in Table II, the furfural obtained by the Youngburg method of analysis was multiplied by 1.71, the average figure given in Kröber's tables[13] for a like calculation. The

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[10] A. D. Dickson, H. Otterson, and K. P. Link, THIS JOURNAL, 52, 775 (1930).

[11] G. E. Youngburg, *J. Biol. Chem.*, 73, 599 (1927).

[12] H. R. Stiles, W. H. Peterson and E. B. Fred, J. Bact., 12, 427 (1926).

[13] C. A. Browne, "A Handbook of Sugar Analysis," John Wiey and Sons. Inc., New York, 1912.

general trend of the figures is toward high values when the uronic acid content is high, and low figures for the samples which contain less uronic acid.

The sixth column in Table II is headed "Pentosans (actual)." Both uronic acids and pentoses will yield furfural when heated with phosphoric acid, If the amount theoretically obtainable from the uronic acid is subtracted from the total furfural a small difference is left. This remainder was calculated to pentosans, and the values are given under the column headed "Pentosans (actual)." The figures vary from 2.2 to 9.2%.

The last column of Table II gives the percentage (ash-free basis) of reducing sugar calculated as glucose which was yielded on hydrolysis of the gums. The amount of reducing substance obtained ranged from 52.8 to 82.2% of the ash-free gum. Although the reducing effect was calculated as glucose, the reduction is not necessarily due to this sugar alone, since other substances such as furfural or uronic acid would likewise reduce Fehling's solution. Our results are not in agreement with those of Grieg-Smith,[8] who reported that the gums of pea and lupine nodule bacteria were hydrolyzed quantitatively to reducing sugar.

Hydrolysis of Gums, and Identification of Sugars by Chemical Means

Tests were made on Preparation 1 (alfalfa nodule bacteria) to ascertain what conditions of hydrolysis gave the maximum yield of sugars. Five per cent. (by weight) sulfuric acid was used as the hydrolytic agent. Although refluxing the acid solution of the gum for ten hours produced the maximum yield of reducing sugar (72.9), autoclaving for two hours at 15 pounds' steam pressure was a more convenient method of hydrolysis and gave only a slightly lower yield of sugar (68.4%). The latter method was therefore adopted as the general procedure. The acid was neutralized with barium carbonate, the barium sulfate filtered off, washed free of reducing sugars and the filtrate evaporated to about 50 cc. At this point decolorization was effected with bone charcoal and the filtrate again evaporated to a small volume. On pouring this sugar solution into four volumes of 95% alcohol, a flocculent precipitate formed at once. This precipitate was probably uronic acid. Ehrlich and von Sommerfeld[14] obtained barium galacturonate from the hydrolysis of pectins at this point. The precipitate gave a strong naphthoresorcinol test for uronic acid. A mucic acid test was negative, *so* that the acid seems to be *glucuronic*. All of the preparations of which the hydrolysis products were studied (Numbers 1, 6, 7, 8) gave strong naphthoresorcinol tests. Work is now in progress to identify this acid by the preparation of its characteristic derivatives.

Hydrolysis **of** Preparation 1.[15] (Alfalfa Nodule Bacteria Gum.)—The carbon content of this preparation was found to be 40.6% when analyzed by the micro-method of Lochte.[16] Analysis for total nitrogen by the Kjeldahl method gave no nitrogen beyond the experimental error.

The gum was hydrolyzed by the procedure already given and glacial acetic acid was added to the concentrated sugar solution. Crystallization took place after several days. The crystals were filtered off, washed with glacial acetic acid, redissolved in a minimum

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[14] F. Ehrlich and R. v. Sommerfeld, *Biochem. Z.*, 168,263 (1926).

[15] The work on the preliminary hydrolyses, the crystallization and identification of glucose was performed by Mr. W. B. Sarles.

[16] H. L. Lochte, THIS JOURNAL, 48,1301 (1926).

quantity of water and again recrystallized after the addition of glacial acetic acid. After filtering and washing, the crystals were dried to constant weight in a vacuum desiccator. The weight of sugar obtained was 0.3158 g. This sugar was dissolved in 25 cc. of water, a drop of ammonia was added to bring about constant rotation and readings were made in a 200-mm. tube at 20°: reading, +7.75° Ventzke scale, $[\alpha]_D^{20}$ +53.2°; $[\alpha]_D^{20}$ for d-glucose, +52.8°.

Hydrolysis of Preparation 7. (Red Clover Nodule Bacteria Gum.)—The sugar was used for qualitative tests, and osazone preparations. Qualitative tests: aniline hydrochloride and phloroglucinol tests for furfural were positive. A uronic acid, as well as a pentose, would yield furfural under the conditions of these tests. Grieg-Smith[8,2] reports that the gums which he examined gave furfural on hydrolysis.

To the sugar in solution, phenylhydrazine hydrochloride and sodium acetate were added in amounts such that the ratio of the three compounds was 1, 2, 3. Yellow crystals formed after seventeen minutes heating in a boiling water-bath. The crystals were filtered off, recrystallized twice from a mixture of pyridine and 50% alcohol and twice from pyridine alone. The crystals occurred in fan-shaped aggregates of yellow needles. The melting point was 204°.

The osazone of glucose was prepared in the same way and recrystallized four time.; from pyridine. The preparation melted at 204°. Browne[13] gives the melting point of phenylglucosazone as 204–205°.

Hydrolysis of Preparation 6.—The phenylosazone of the reducing sugar was prepared as previously indicated and purified by six recrystallizations from pyridine. Its melting point was 204°.

Qualitative tests for mannose (hydrazone test) and fructose (Seliwanoff test) were made on the sugar solution after hydrolysis of the gum with negative results in both tests. When mannose and fructose equivalent to 5% of the total reducing sugar present were added to the hydrolysis product, positive tests were obtained. It is probable, therefore, that if these sugars are contained in the gum molecule, they constitute only a small percentage of the total sugar.

Hydrolysis of Preparation 8. (Pea Nodule Bacteria Gum.)—The phenylosazone of the sugar was prepared, and recrystallized seven times from pyridine. The melting point was 204°. Qualitative tests were made for mannose and fructose as under the hydrolysis of Preparation **6,** and both tests were negative.

Identification of Sugar by Fermentation Tests

The above evidence shows that glucose is a constituent of the gum, but that fructose and mannose are absent. The work of Grieg-Smith[8,2] indicates the possibility of the presence of galactose. Pentoses may also be present, as was suggested by the furfural figures (Table II). The chemical determination of such a mixture of sugars would be difficult, if not impossible. It should be possible, however, by means of fermentation tests to prove the presence or absence of these sugars. This method of sugar determination has been suggested and used in various ways. Kluyver[17] used yeast alone for the sugar determination, while Sherrard and Blanco[18] used yeast fermentation followed by fermentation with bacteria. By means of galactose and non-galactose fermenting yeast, the presence or absence of this sugar could be demonstrated. Likewise, the use of twa

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[17] A. J. Kluyver, "Biochemische Suikerbepalingen," Thesis, Delft, 1914, **223** p.

[18] E. C. Sherrard and G. W. Blanco, **Ind.** *Eng. Chem.*, **15,611** (1923).

strains of bacteria, one fermenting xylose but not arabinose, the other using arabinose and not xylose, might be used in the determination and identification of any pentoses present. The organisms selected for this purpose were the following: *Schizosaccharomyces pombe*, *Saccharomyces cerevisiae*, yeast, Honey B and lactic acid-producing organisms Nos. 19 and 36. The *Saccharomyces cerevisiae* yeast was obtained from a single cell isolation. The yeast called "Honey B" was isolated from fermenting honey. *Schizosaccharomyces pombe* and Honey *B* ferment glucose but not galactose, while the *Saccharomyces cerevisiae* ferments both glucose and galactose. Culture No. 36 ferments xylose, but leaves arabinose untouched, while Culture 19 ferments arabinose, but not xylose. Analysis of a mixture of known sugars by means of these organisms was first made to determine whether the method would give satisfactory results. The sugar solutions were added to a 10% extract of fresh starch-free yeast and the PH adjusted to 5.2; 10-cc. samples of this solution were pipetted into test-tubes, the tubes plugged with cotton and sterilized. Inoculations of the tubes were made as indicated in Table III, and after eight days' incubation at 28° the remaining sugar was determined in 1 cc. drawn from each culture tube. The remaining liquid was resterilized, sterile calcium carbonate added and inoculated with the pentose-fermenting bacteria. Sugar analyses were made on the cultures after ten days' incubation at 37°. Table III gives the results of the experiment, and indicates that satisfactory checks can be obtained by this method. The slight decrease in sugar in the uninoculated controls (Tubes 7 and *8)* is probably due to loss on sterilization.

TABLE III

ANALYSIS OR KNOWN MIXTURES OR SUGAR BY MEANS OF YEASTS AND BACTERIA

	Tubes 1 and 2		Tubes 3 and 4		Tubes 5 and 6		Tubes 7 and 8	
	Yeast fermentation							
Yeast	*Saccharomyces cerevisiae*		*Schizosaccharomyces pombe*		Honey *B*		Uninoculated	
Type of sugar fermented	Glucose and galactose		Glucose		Glucose		....	
	1	2	3	4	5	6	7	8
Before, mg.	101.5	101.5	101.5	101.5	101.5	101.5	101.5	101.6
After, mg.	27.3	26.6	49.9	49.2	48.7	47.8	99.7	99.7
Should be present, mg.	24.2	24.2	49.0	49.0	49.0	49.0	101.5	101.5
	Bacterial fermentation							
Bacteria	No. 36	No. 19	No. 36	No. 19	No. 36	No. 19	Uninoculated	
Type of sugar fermented	Xylose	Arabinose	Xylose	Arabinose	Xylose	Arabinose		
Before, mg.	27.3	26.6	499	49.2	48.7	47.8	99.7	99.7
After, mg.	11.8	13.6	12.4	12.4	13.4	12.5	94.3	95.4
Should be present, mg.	11.4	12.8	11.4	12.8	11.4	12.8	101.5	101.5

The sugar solution in each tube contained the following amounts of sugar: glucose, 52.5 mg.; galactose. 24.8 mg.; xylose, 12.8 mg.; arabinose, 11.4 mg.; total, 101.5 mg.

The fermentation test just described was applied to the hydrolyzed solution of Preparations 6 and 8.

Fermentation Test on Preparation 6. (Red Clover Nodule Bacteria Gum.)--0.532 g. of sugar in solution was taken for the fermentation test. This solution was concentrated, yeast water added and the P_H adjusted to 5.2; 10-cc. portions of this solution were then pipetted into each of four test-tubes and the tubes sterilized. Three of the tubes were inoculated with yeast which would ferment only glucose, Honey B and *Schizosaccharomyces pombe*, and the other one with the yeast which would ferment both glucose and galactose, *Saccharomyces cerevisiae*. The tubes were incubated at 28°. Eight days after inoculation the cultures were made up to 10 cc., and 1 cc. was removed. This was then made up to 5 cc., and 1 cc. of this last dilution taken for micro sugar analysis.

As has been indicated, the presence of pentoses was suggested by the furfural data (Table II). The pentoses present would be most likely to be arabinose and xylose, it being more probable that there would be only one of these in the molecule. In order to decide this question, the solutions fermented by the yeast were submitted to bacteria fermentations. Yeasts do not normally attack pentoses, especially in the presence of a hexose, so that the pentose, if present, should still be in solution. The control fermentation of the mixture of known sugars showed that the pentoses were not attacked by the yeast. The remaining sugar solution after the yeast fermentation was again sterilized in tubes and sterile calcium carbonate added. Pure cultures of the lactic acid bacteria were inoculated into the tubes of sugar solution, and incubated at 38° for twelve days. At the end of that time the contents of each tube were made up to 10 cc., and 1 cc. of this solution was taken for micro sugar analysis.

The results of the two fermentations are given in Table IV. The yeast fermentation gave results which showed that the hexose was glucose, or that if galactose was also present, it was so in insignificantly small amounts. The difference between the amount of sugar fermented by the two bacterial cultures was so slight as not to permit the conclusion that pentoses were present. Typical fermentation data are given in detail in Table IV. The extent of recovery of galactose when added to the gum sugar solution was tested in later experiments: 98–100% was destroyed by the galactose-fermenting yeast and 3.8% fermented by the non-galactose fermenting yeast.

TABLE IV

FERMENTATION OF SUGARS FROM PREPARATION 6 (RED CLOVER ROOT NODULE BACTERIA GUM)

	Tube 1	Tube 2	Tube 3	Tube 4
	Yeast fermentation			
Yeast	Honey B	Honey B	*Saccharomyces cerevisiae*	*Schizosaccharomyces pombe*
Type of sugar fermented	Glucose	Glucose	Glucose and galactose	Glucose
Before, mg.	267	267	267	267
After, mg.	26.6	24.7	22.3	26.6
Sugar fermented, mg.	240.4	242.3	244.7	240.4
	Bacterial Fermentation			
Bacteria	No. 36	No. 19	No. 36	No. 19
Type of sugar fermented	Xylose	Arabinose	Xylose	Arabinose
Before, mg.	26.6	24.7	22.3	26.6
After, mg.	16.0	16.6	15.6	16.8
Sugar fermented, mg.	10.6	8.1	6.7	9.8

A second fermentation experiment (data not given) was conducted in the same manner as the one above. *Saccharomyces cerevisiae* and *Schizosaccharomyces pombe* were the yeasts used in this experiment, since Honey B grew more slowly and gave no additional information. The percentage of sugar fermented by the yeasts was higher in this experiment than in the first. The reducing substance remaining after the yeast fermentation is probably uronic acid, which is generally believed to be unfermentable by yeasts. The controls of known sugars show that the yeast fermentation is complete to the extent of nearly one hundred per cent. In the gum sugar solutions the bacteria do not, then, ferment only the portion of the hexose left by the yeast, but also a part of some other reducing substance still in solution. It may be possible that they are able to ferment the uronic acid. At the same time this fermentation does not indicate the presence of a pentose. The difference in percentage of fermentation of the sugar by the yeast between the first and second fermentations may be explained by the fact that in the first fermentation calcium carbonate had been used to neutralize the acid after hydrolysis of the gum, while in the second fermentation, barium carbonate was used. Since barium salts are generally less soluble than calcium salts, there was probably more complete removal of the uronic acid when barium carbonate was used. The reducing material left after the yeast fermentation appears to be the uronic acid, or its salts.

In the second bacterial fermentation of the sugars produced by hydrolysis of Preparation 6, the sugar contents of only two of the six tubes used in the fermentation could be determined. The other four tubes contained some material which prevented the appearance of the usual iodine end-point. In these cases, after titration to the end-point, the blue color reappeared.

Fermentation Test on Preparation 8. (Pea Root Nodule Bacteria Gum.)—The fermentation test was conducted in the same manner as was given under the fermentation of Preparation 6, two complete sets of fermentations being made in this case as in the one above. In Table V it will be seen that the extent of fermentation of the sugar by yeast is not as great as it was on the sugars from Preparation **6.** The presence of galactose is not indicated by the results obtained.

The percentage of hexose fermented by the yeast in the second fermentation (Prepn. 8) was larger than it was in the first. This is probably due, as seemed to be the case with the fermentation of sugars from Preparation 6, to the use of barium carbonate instead of calcium carbonate as the neutralizing agent of the hydrolysate in the second fermentation.

The bacterial fermentation in the second fermentation gave results which did not indicate the presence of a pentose.

Table V gives a summary of the results of the fermentations on the hydrolyzed gum of Preparations 6 and 8. The figures given under each preparation are the average of two complete fermentation tests like that represented in Table IV. **A** comparison of the percentages of sugar fermented by the galactose and non-galactose fermenting yeast indicates that if galactose is present at all, it is so in amounts of 1% or less. Likewise, the bacterial fermentations demonstrated that there is less than 1% of **a** pentose present, and it is likely that no pentose is present at all. The small differences between these fermentations cannot safely be attributed to any other cause than the biological variation inherent in such a method. The results of the yeast fermentation tests show that the hexose obtained on hydrolysis of the gum of both red clover and pea root nodule bacteria gum was glucose. The bacterial fermentations do not give evidence of the presence of a pentose sugar.

TABLE V

THE COMPOSITION, AS SHOWN BY FERMENTATION TESTS, OF THE GUM SUGAR OBTAINED FROM HYDROLYSIS OF PREPARATIONS 6 AND 8

		Preparation 6 Percentage of total sugar		Preparation 8 Percentage of total sugar	
Yeast	**Glucose fermenting**	92.6	93.1	82.9	83.2
	Galactose and glucose fermenting	93.6		83.6	
Bacteria	**Xylose fermenting**	3.2	3.0	5.6	5.2
	Arabinose fermenting	2.8		4.7	
Unfermented reducing substance			4.3		11.6
			100.4		100.0

Conclusions

Root nodule bacteria of three cross-inoculation groups were grown in pure culture on synthetic media, and the gum produced was precipitated with acetone. The gum of the root nodule bacteria of alfalfa, *Rhizobium meliloti* 100, was nitrogen-free, The carbon content of this gum was variable, being 40.6% in one sample, and 36.4% in another. Glucose was crystallized from the gum solution after hydrolysis, and identified by its specific rotation (+53.2°).

Glucosazone was prepared from hydrolyzed gum produced by pure cultures of red clover root nodule bacteria, *Rhizobium trifolii* 205 and 201, and pea root nodule bacteria, *Rhizobium leguminosarum* 311. Fermentation tests of the sugar from these two gums by pure cultures of known yeasts also indicated that the sugar was glucose. Fermentation tests by pure cultures of pentose-fermenting lactic acid bacteria showed the absence of a pentose sugar.

The gums of *Rhizobium meliloti* 100, *Rhizobium trifolii* 205 and 201, and *Rhizobium leguminosarum* 311 contain uronic acid in amounts varying between 4.1 and 25.3% ash-free basis.

All of the results up to the present time indicate that these gums of the root nodule bacteria are complexes of glucose and a uronic acid, probably glucuronic acid.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE EXPERIMENTAL STATION, HERCULES POWDER COMPANY]

THE VISCOSITIES OF GLYCEROL TRINITRATE AND CERTAIN RELATED GLYCOL NITRIC ESTERS[1]

BY J. MERRIAM PETERSON

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Introduction

During a general study of glycerol trinitrate and certain glycol dinitrates need arose for data on the viscosities of these substances. A search of the literature revealed only a small amount of data and the values which were reported covered a very limited temperature range. It was then necessary to undertake the task of determining these viscosities and determinations were made at five-degree intervals over the temperature range 10 to 60°, inclusive, on highly purified samples of the following esters: propylene glycol dinitrate, ethylene glycol dinitrate, trimethylene glycol dinitrate, diethylene glycol dinitrate and glycerol trinitrate.

Naoúm[2] tabulates viscosities at 20° for four of the esters included in the present investigation. The data are given in seconds required to run 5 cc. out of a 10-cc. pipet, as follows: propylene glycol dinitrate, 5.0 seconds; ethylene glycol dinitrate, 5.0 seconds; trimethylene glycol dinitrate, 5.5 seconds, and glycerol trinitrate, 12.5 seconds. A calibration of the pipet with water required 4.5 seconds for the time of flow. The results indicate that the viscosities of the esters are only slightly greater than the viscosity of water, with the exception of glycerol trinitrate, which appears to be about 2.5 times as viscous. More reliable values were determined by Rinkenbach[3] for glycerol trinitrate and diethylene glycol dinitrate between 15 and 27°. In an earlier communication[4] he gives values for the viscosities of ethylene glycol dinitrate and glycerol trinitrate at 23.6°. These values are included for comparative purposes in the tables of viscosities for the present work.

Materials.—The nitric esters were prepared from the corresponding glycols by nitration with a mixture of nitric and sulfuric acids as described by Crater.[5] After neutralization, washing and thorough drying, determinations of the specific gravity and nitrogen content were made for each compound. The results given in Table I indicate compounds of a high degree of purity.

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[1] Presented before the Division of Inorganic and Physical Chemistry at the 76th Meeting of the American Chemical Society, Minneapolis, Minnesota, September 9 to 13, 1929.

[2] Naoúm, "Nitroglycerin und Nitroglycerin Sprengstoffe," Julius Springer, Berlin, 1924, p. 234. Also Lawrie, "Glycerol and the Glycols" The Chemical Catalog Company, Inc., New York, 1928, p. 340

[3] Rinkenbach, *Ind. Eng. Chem.*, 19,925 (1927).

[4] Rinkenbach, *ibid.*, 18,1195 (1926).

[5] Crater, *Ind. Eng. Chem.*, 21,674 (1929).

TABLE I

SPECIFIC GRAVITY AND NITROGEN CONTENT OF ESTERS

Material	Formula	Specific gravity 15°/15° Pound	Specific gravity 15°/15° Literature	Nitrogen, % Found	Nitrogen, % Calcd.
Propylene glycol dinitrate	$C_3H_6(NO_3)_2$	1.3939	1.368 (20°)[a]	16.85	16.87
Ethylene glycol dinitrate	$C_2H_4(NO_3)_2$	1.4956	1.4963"	18.31	18.42
Trimethylene glycol dinitrate	$C_3H_6(NO_3)_2$	1.4703	1.393 (20°)[a]	16.81	16.87
Diethylene glycol dinitrate	$C_4H_8O(NO_3)_2$	1.3901	1.3908[b]	14.24	14.29
Glycerol trinitrate	$C_3H_5(NO_3)_3$	1.5978	1.599"	18.42	18.51

[a] Naoúm. [b] Rinkenbach.

Method.—A Bingham and Jackson[6] viscometer was used to determine the viscosities of the esters. While this instrument is of the pipet type, it eliminates most of the objections so common to many of the pipet methods and is capable of giving absolute values for viscosity in c. g. s. units. **A** correction may be applied when necessary for the kinetic energy of the liquid measured, a correction which is too often overlooked or neglected in viscosity determinations.

The method consists essentially in measuring the time of flow of a given volume of liquid (about 4 cc.) at a specified temperature and under a known constant pressure, through a capillary tube which has been previously calibrated. Details of the instrument and method may be found by referring to the original paper.

Temperature was held automatically to ±0.1° of that desired by means of a large, well-stirred water thermostat controlled by a mercury regulator in conjunction with a relay and knife type lagless heater. Pressure was supplied from a tank filled to any desired pressure directly from the compressed air line and was measured by an open-end mercury manometer. Corrections were made to reduce the manometer readings to mm. of mercury at 0°. The tank was of sufficient size so that there was no perceptible drop in pressure resulting from the small quantity of air removed during a determination. Time measurements were made with a stop watch accurate to 0.2 second.

Calibration and Calculations.—The viscosities were calculated by the formula

$$\eta = Cpt - \frac{C'\rho}{t} \qquad (1)$$

where η is viscosity of the substance in c. g. s. units (poises), C and C are constants of the individual instrument, t is time in seconds, p is pressure in grams per square centimeter and p is density of sample in grams per cubic centimeter.

The second term of the right-hand member of the above equation is the

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[6] Bingham and Jackson, Sci. Papers of the Bureau of Standards, No. 298 (1917)

kinetic energy correction, which is kept small by keeping *t* comparatively large. For this reason C' and p need not be known with great accuracy. The density of the ester used in this correction was calculated from the specific gravity values given in Table I.

The value of the constant C' was determined from the dimensions of the instrument as outlined by Bingham.[7] The value of the constant C was obtained by filling the viscometer with freshly distilled, dust-free water and determining the time of flow at 20°. The value used for the viscosity of water at 20° was **1.005** centipoises. Table II lists the constants of the two instruments used.

TABLE II

CONSTANTS OF VISCOMETERS

Viscometer	Capillary length. mm.	Radius, mm.	Volume of bulb, cc. (20°)	C	C'
Instrument 1	121.0	0.169	4.08	6.416×10^{-7}	0.01504
Instrument 2	120.0	0.244	4.02	2.851×10^{-6}	0.01494

Data.—In Tables III, IV, V, VI and VII are tabulated summaries of the viscosity data obtained. Four to six determinations were made at each temperature for each substance; the number in each case is given in the first column of each table. The temperature of the liquid **at** the time of the determination is given in Col. 2, the average of the values for the separate viscosity determinations is tabulated in Col. **3 and** the maximum deviation of the individual determinations from the average viscosity is recorded in Col. 4. The fluidity in rhes (reciprocal viscosity in poises) was calculated and is given in Col. 5. The values for the viscosities of the esters at the corresponding temperatures as reported by previous investigators, Rinkenbach (indicated by R) and Naoúm (indicated by N),

TABLE III

VISCOSITIES OF PROPYLENE GLYCOL DINITRATE

Detns.	Temp., °C.	Av. η, poises	Max. dev. from mean (in poises)	Av. φ, rhes	Reported η, poises
6	10.0	0.0556	0.0001	18.0	
5	15.0	.0476	.0001	21.0	
4	20.0	.0407	.0002	24.6	0.0155 (N)
5	25.0	.0355	.0000	28.2	
4	30.0	.0314	.0000	31.9	
4	35.0	.0278	.0001	36.0	
4	40.0	.0246	.0000	40.7	
4	45.0	.0221	.0000	45.3	
4	50.0	.0203	.0000	49.3	
4	55.0	.0183	.0000	54.6	
4	60.0	.0171	.0000	58.5	

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[7] Bingham, "Fluidity and Plasticity," McGraw-Hill Book Company. Inc., New York, 1922, p. 295.

TABLE IV

VISCOSITIES OF ETHYLENE GLYCOL DINITRATE

Detns.	Temp., °C.	Av. η, poises	Max. dev. from mean (in poises)	Av. φ, rhes	Reported poises
4	10.0	0.0573	0.0002	17.5	
4	15.0	.0487	.0001	20.5	
4	20.0	.0421	.0001	23.8	
	23.6				0.0166 (N) 0.0363 (K)
4	25.0	.0369	.0001	27.1	
4	30.0	.0329	.0001	30.4	
4	35.0	.0292	.0000	34.3	
4	40.0	.0260	.0001	38.5	
4	45.0	.0236	.0001	42.5	
4	50.0	.0214	.0001	46.7	
4	55.0	.0195	.0001	51.3	
4	60.0	.0182	.0001	54.9	

TABLE V

VISCOSITIES OF TRIMETHYLENE GLYCOL DINITRATE

Detns.	Temp., °C.	Av. η, poises	Max. dev. from mean (in poises)	Av. φ, rhes	Reported poises
4	10.0	0.0851	0.0001	11.8	
4	15.0	.0706	.0002	14.2	
4	20.0	.0597	.0002	16.8	0.0179 (N)
4	25.0	.0501	.0002	20.0	
4	30.0	.0436	.0002	22.9	
4	35.0	.0388	.0002	25.8	
4	40.0	.0344	.0001	29.1	
4	45.0	.0310	.0001	32.3	
4	50.0	.0282	.0001	35.5	
4	55.0	.0258	.0001	38.8	
4	60.0	.0233	.0001	42.9	

TABLE VI

VISCOSITIES OF DIETHYLENEGLYCOL DINITRATE

Detns.	Temp., °C.	Av. η, poises	Max. dev. from mean (in poises)	Av. φ, rhes	Reported poises
4	10	0.119	0.003	8.40	
5	15	.0970	.0002	10.3	0.099 (R)
	17.5				.085 (R)
5	20.0	.0808	.0002	12.4	.078 (R)
	22.5				.073 (R)
4	25.0	.0673	.0001	14.9	.070 (R)
	27.0				.066 (R)
4	30.0	.0573	.0000	17.5	
4	35.0	.0496	.0001	20.1	
4	40.0	.0437	.0000	22.9	
5	45.0	.0383	.0001	26.1	
4	50.0	.0351	.0001	28.6	
4	55.0	.0306	.0001	32.7	
4	60.0	.0275	.0001	36.4	

TABLE VII

VISCOSITIES OF GLYCEROL TRINITRATE

Detns.	Temp., °C.	Av. η, poises	Max. dev. from mean (in poises)	Av. φ, rhes	Reported η, poises	
4	10	0.692	0.002	1.45		
4	15	.491	.000	2.04	0.511 (R)	
	17.5				.423 (R)	
4	20.0	.360	.000	2.78	.355 (R)	0.043 (N)
	22.5				.303 (R)	
	23.6				.288 (R)	
5	25.0	.270	.000	3.70	.283 (R)	
	27				.258 (R)	
4	30	.210	.000	4.76		
5	35	.168	.001	5.95		
4	40	.136	.000	7.35		
4	45	.112	.000	8.93		
6	50	.0938	.0002	10.7		
4	55	.0792	.0001	12.6		
4	60	.0680	.0000	14.7		

are given in the last column. Naoúm's values were converted to c. g. s units, for comparative purposes, by the equation

$$\eta = \eta_0 \frac{\rho t}{\rho_0 t_0} \qquad (2)$$

where η, ρ and t represent the viscosity, density and time of flow, respectively, for the unknown and η_0, ρ_0 and t_0 represent similar quantities for the standard substance (water). η_0 was taken as 0.0100 poises at 20° and ρ_0 was taken as 1.0.

Discussion of Results

Pressure measurements ranged from 10.04 to 163.23 cm. of mercury. The maximum error was probably not greater than 0.2 mm., which would result in an error of not more than 0.2% in the calculated viscosities even at the lower pressures. The times of flow varied from 490.6 to 45.6 seconds. Except in the case of ethylene glycol dinitrate, however, the times of flow were over 200 seconds. An error of 0.2 second in the time measurements would cause an error of not more than 0.1% in the calculated values, except with ethylene glycol dinitrate, where the error may reach 0.4%. By using an accurately controlled thermostat and waiting several minutes for temperature equilibrium of the sample to be reached after each change in the thermostat temperature, the error from this source was negligible. The total error in the final results is thought to be not greater than 0.25% for the individual determinations and this appears to be justified by an examination of the maxium deviation from the mean as given in the tables.

The average viscosities when plotted against temperatures give smooth curves, as shown in Fig. 1. Considering the fact that the plotted viscosities are the mean of four to six closely agreeing, duplicate values, the resulting curves should be in error by not more than 0.1%. This is within the limitations associated with the purification of the compounds studied.

It is interesting to note that the values are almost the same for propylene glycol dinitrate and ethylene glycol dinitrate, while the values for the two isomers, propylene glycol dinitrate and trimethylene glycol dinitrate differ considerably. Such a marked increase in the viscosity of glycerol trinitrate might not have been expected. Because of its large coefficient of viscosity with temperature in this temperature range, the upper part of the viscosity curve, Fig. 1, was cut off. The unplotted values, however, fall upon as smooth a curve as do the plotted values.

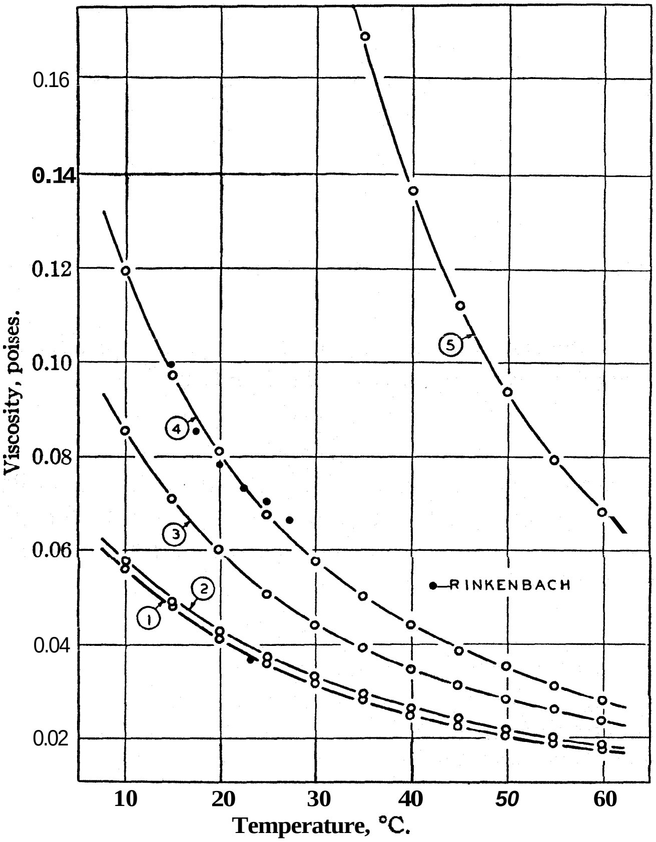

Fig. 1.—viscosity-temperature curves of esters: 1, propylene glycol dinitrate; 2, ethylene glycol dinitrate; 3, trimethylene glycol dinitrate; 4, diethylene glycol dinitrate; 5, glycerol trinitrate.

The results herein reported agree quite satisfactorily with those reported by Rinkenbach. The values given by Naoúm are worthy of special attention. They are quite typical of many values reported in the literature obtained by arbitrary methods where the viscometer used is calibrated by a substance which differs greatly from the unknown substance, and no kinetic energy corrections are made for rapid rates of flow. While such results are usually intended only for relative values, they are often decidedly misleading. In the present case it would be assumed from the times of flow that glycerol trinitrate is approximately 2.5 times as viscous as water at 20°, or four times as viscous if the viscosity is calculated by Equation 2. The results obtained during this investigation show the ratio to be about 36 to 1.

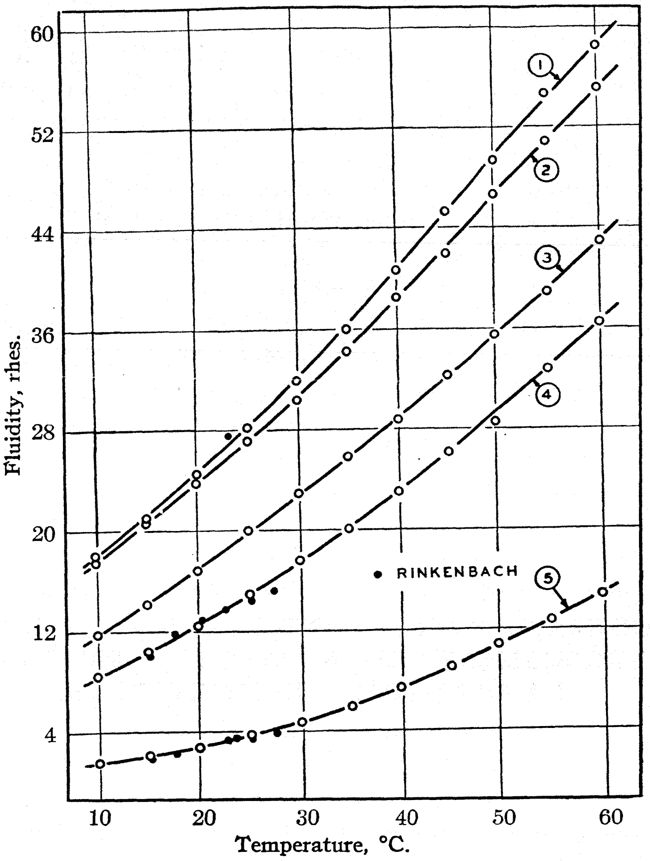

Fig. 2.—Fluidity–temperature curves of esters: 1, propylene glycol dinitrate; 2, ethylene glycol dinitrate; 3, trimethylene glycol dinitrate; 4, diethylene glycol dinitrate; 5, glycerol trinitrate.

Since fluidities (reciprocal viscosities) are more convenient to use in certain cases than viscosities, they are included in the tables and are plotted in Fig. 2. The resulting curves deviate somewhat from straight lines, a slight sag being noted in each case.

Plotting log viscosities against temperatures resulted in curves which deviated from straight lines to about the same extent as did the fluidity curves.

The fluidity curves, however, approach straight lines nearly enough so that they may be easily extended to temperatures beyond those actually determined, at least to those temperatures of importance in the commercial application of the esters.

Acknowledgment.—The author wishes to express his appreciation of the assistance of W. deC. Crater, who kindly prepared the samples used in this investigation.

Summary

The viscosities of highly purified samples of propylene glycol dinitrate, ethylene glycol dinitrate, trimethylene glycol dinitrate, diethylene glycol dinitrate and glycerol trinitrate were measured in c. g. s. units (poises) at five-degree intervals over the temperature range 10 to 60°, inclusive, and the results compared with previously reported values. The corresponding fluidities were calculated and reported.

KENVIL, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON HYDANTOINS. XLIX. A NEW REARRANGEMENT LEADING TO THE FORMATION OF 4-AMINOHYDANTOIN DERIVATIVES

BY R. M. HERBST[1] AND T. B. JOHNSON

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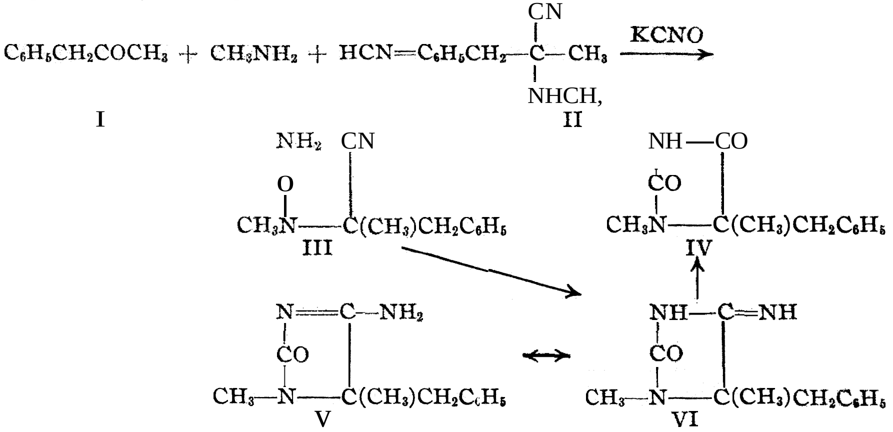
In the course of an investigation dealing with the synthesis of 5,5-dialkylated hydantoins from ketones, the authors had occasion to study the applicability of a series of reactions suggested for the preparation of 1,5,5-trialkyl-hydantoins. Tiemann and Piest[2] first showed that the Strecker synthesis of a-amino acids could be modified to include N-alkylamino acids if an amine is used in place of ammonia in the reaction with aldehyde or ketone cyanhydrins. Biltz and Slotta[3] applied this phase of the Strecker–Tiemann reaction to the synthesis of 1-alkyl-hydantoins. We have now employed the same series of reactions described by Biltz and Slotta under modified experimental conditions for the preparation of 1,5,5-trialkyl-

[1] Eli Lilly Company Graduate Scholar, 1928–1929.

[2] Tiemann and Piest, *Ber.*, 14, 1982 (1881); 15, 2028 (1882).

[3] Biltz and Slotta, *J. prakt. Chem.*, **113**, 233 (1926).

hydantoins. The method of operating is illustrated by the synthesis of 1,5-dimethyl-5-benzylhydantoin from methyl benzyl ketone which is expressed by the equations



$$\underset{I}{C_6H_5CH_2COCH_3} + CH_3NH_2 + HCN = \underset{II}{C_6H_5CH_2-\underset{NHCH_3}{\overset{CN}{C}}-CH_3} \xrightarrow{KCNO}$$

A careful study of these reaction changes has now revealed a mechanism of ring formation which has not been observed, hitherto, in the hydantoin series. The a-methylureido-a-methyl-/3-phenylpropionitrile (III), prepared as an intermediate in this synthesis, undergoes a molecular rearrangement on boiling in water solution to form 1,5-dimethyl-5-benzyl-4-aminohydantoin (V or VI). The transformation is perfectly analogous to that which was observed by Pschorr,[4] who encountered a similar reaction in the synthesis of α-aminoquinolines from o-aminocinnamylcyanides. Traube[5] and Conrad[6] have described analogous rearrangements leading to the formation of ring compounds in the synthesis of barbituric acid and derivatives.

Jongkees[7] has prepared 4-iminohydantoin-1-acetamide, in which the imino group is easily replaced by oxygen by warming with dilute hydrochloric acid. His technique involved cyclization in ammoniacal solution. Our compound shows a much greater stability than Jongkees' hydantoin, and is not affected by boiling even with fairly strong hydrochloric acid. The amino group can be replaced with oxygen, however, by treatment with nitrous acid, analogous to the conversion of cytosine into uracil studied by Kossel and Steudel[8] and later by Wheeler and Johnson.[9] These facts favor the amino V, in preference to the imino structure VI, for the cyclic compound.

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[4] **Pschorr,** *Ber.,* 31, 1289 (1898).

[5] **Traube,** ibid., 33, 1371 (1900); *Ann.,* 331, 64 (1904).

[6] Conrad, *ibid.,* 340, 310 (1905).

[7] Jongkees, *Rec. trav. chim.,* **27,** 287–326 (1908).

[8] Kossel and Steudel, Z. *physiol. Chem.,* 38, 49 (1903).

[9] Wheeler and Johnson, Am. *Chem. J.,* *29,* **492** (1903).

This rearrangement suggests a possible reaction mechanism for the conversion of ureido-nitriles into hydantoins by means of aqueous hydrochloric acid. Generally this transformation is expressed as one involving, first, hydrolysis of the nitrile to the corresponding hydantoic acid, and then a molecular condensation to form the hydantoin. According to the new conception the change to ring structure first involves a formation of the intermediate imino compound VI, which is unstable in the presence of strong hydrochloric acid and is decomposed immediately, giving the normal hydantoin. On the other hand, in the absence of hydrochloric acid, or under conditions where we have a low hydrogen-ion concentration, the imino compound may undergo tautomerization to form the isomeric and more stable aminohydantoin V, which is not attacked by acids. In the above rearrangement we have an excellent example apparently of this tautomeric change, and it is a molecular transformation which possesses considerable biochemical interest. This tautomerization is undoubtedly influenced by the character of the groups substituted in the hydantoin ring on nitrogen and carbon.

The rapidity with which hydantoins are formed from ureido-nitriles, the reaction being almost instantaneous, lends support to the belief that something other than the hydrolysis of a cyanide group to carboxyl is involved in this reaction. The unique behavior of the ureido-nitrile suggests a mechanism of reaction which is far more general than we have hitherto realized.

Experimental

α-Methylamino-α-methyl-β-phenylpropionitrile, II.—Seven and nine-tenths cc. (0.2 mole) of anhydrous hydrocyanic acid and 6.2 g. (0.2 mole) of dry methylamine are dissolved in a thoroughly cooled solution of 26.8 g. (0.2 mole) of methyl benzyl ketone in 25 cc. of absolute ethyl alcohol. After the solution has stood at room temperature in a well-stoppered bottle for twenty-four hours, it is taken up in 200 cc. of ether, washed with cold water and dried over sodium sulfate. The hydrochloride of α-methylamino-α-methyl-β-phenylpropionitrile is then precipitated by passing dry hydrogen chloride into the ethereal solution. It separates first as an oil, which on continued treatment with hydrogen chloride changes to a colorless, crystalline solid, melting at 106–108°[10] with decomposition, after sintering at 102°. The yield of hydrochloride is 35 g. (85%). The hydrochloride decomposes slowly on standing, and cannot be kept over long periods. Heating in non-anhydrous solvents causes methylamine hydrochloride and hydrocyanic acid to split off with regeneration of the ketone.

Anal. Calcd. for $C_{11}H_{15}N_2Cl$: N, 13.30. Found: N, 13.14, 13.09

The free methylamino-nitrile, obtained by evaporating the solvent from an ethereal solution at room temperature under reduced pressure, decomposes easily on heating, and cannot be distilled even in vacuo without serious decomposition.

α-Methylureido-α-methyl-β-phenylpropionitrile, III.—During the course of an hour 25 g. of finely ground potassium cyanate is added to a cold suspension of 35 g. of α-methylamino-α-methyl-β-phenylpropionitrile hydrochloride in 100 cc. of glacial acetic acid. After standing in a cool place for fifteen hours, the reaction mixture is poured into

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[10] All melting points are corrected.

500 cc. of ice water. On standing in the refrigerator, **α-methyl-ureido-α-methyl-β-phenylpropionitrile** separates as a flocculent white solid, which is filtered off through a Biichner funnel, washed with water and air-dried. The yield of crude material is 28 g. (77.5%). It crystallizes from 50% alcohol in colorless needles, melting at 130–131°.

Anal. Calcd. for $C_{12}H_{15}ON_3$: N, 19.35. Found: N, 18.91, 18.93.

1,5-Dimethyl-5-benzylhydantoin, IV.—Twenty-eight grams of crude a-methyl-ureido-α-methyl-β-phenylpropionitrile is suspended in 100 cc. of 20% hydrochloric acid. On warming the methylureido-nitrile dissolves and the hydantoin begins to precipitate almost immediately. After heating for one hour on the steam-bath, the suspension is cooled, filtered through a Biichner funnel and the residue washed with cold water. The yield of crude hydantoin is 23 g. (82%). Recrystallization from 50% alcohol. decolorizing with norite if necessary, yields a product melting at 134–135°.

Anal. Calcd. for $C_{12}H_{14}O_2N_2$: N, 12.84. Found: N, 12.92, 12.81.

An attempt to decompose the hydantoin to the corresponding methylamino acid was unsuccessful. After refluxing 5 g. of the hydantoin for one hundred hours with saturated barium hydroxide solution, 4.5 g. of the unchanged hydantoin was recovered.

A crystalline sodium salt is formed when a mixture of a small amount of the hydantoin with an equivalent amount of a 5% solution of sodium hydroxide in 95% alcohol is evaporated in a vacuum desiccator. Solutions of mercuric chloride, calcium chloride and magnesium sulfate precipitate the corresponding salts when added to aqueous solutions of the sodium salt of the hydantoin, The mercury salt precipitates as a flocculent white solid, whereas the calcium and magnesium salts separate as colorless needles.

1,5-Dimethyl-5-benzyl-4-aminohydantoin.—When a solution of or-methylamino-α-methyl-β-phenylpropionitrile in hot water is boiled momentarily, 1'5-dimethyl-5-benzyl-4-aminohydantoin crystallizes out on cooling in a practically quantitative yield, in the form of small, colorless needles, melting at 267–268° with charring.

Anal. Calcd. for $C_{12}H_{15}ON_3$: N, 19.35. Found: N, 19.32, 19.27.

The aminohydantoin is readily soluble in dilute mineral acids, but insoluble in alkalies, which precipitate it unaltered from its solutions in acids. Boiling with acids or alkalies does not affect the aminohydantoin. It forms a characteristic mono-hydrc-chloride and picrate.

On treating with nitrous add, as described by Kossel and Steudel[8] for the ton-version of cytosine to uracil, an acidic compound is obtained, crystallizing from 50% alcohol in plates and melting at 134–135°. Mixed with 1,5-dimethyl-5-benzyl-hydantoin the melting point is unchanged

The hydrochloride of **1,5-dimethyl-5-benzyl-4-aminohydantoin** is prepared by pouring a solution of the aminohydantoin in 95% alcohol saturated with hydrogen chloride into dry ether. On standing the hydrochloride precipitates as a colorless crystalline solid, melting at 218–223° with decomposition.

Anal. Calcd. for $C_{12}H_{16}ON_3Cl$: N, 16.57; Cl, 14.00. Found: N, 16.65; Cl, 13.93.

The picrate of **1,5-dimethyl-5-benzyl-4-aminohydantoin** crystallizes as yellow needles when a solution of equal amounts of the aminohydantoin and picric acid in a slight excess of boiling water is cooled. After recrystallization from 50% alcohol it melts at 226–227° with decomposition.

Anal. (Kjeldahl–Gunning). Calcd. for $C_{18}H_{18}O_8N_6$: N, 18.83. Found: N, 18.97.

Summary

1. 1,5-Dimethyl-5-benzylhydantoin and its 4-amino derivative have been prepared.

2. A new rearrangement leading to hydantoin derivatives substituted in the 4-position with an amino group has been described.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE MECHANISM OF CARBOHYDRATE OXIDATION. XII. THE ACTION OF POTASSIUM HYDROXIDE ON *l*-ARABINOSE AND d-XYLOSE

BY WM. LLOYD EVANS AND ROLLIN FRANCIS CONAWAY

RECEIVED JUNE 6, 1930 PUBLISHED SEPTEMBER 5, 1930

When the hexose sugars, glucose, mannose, fructose and galactose are treated with aqueous solutions of potassium hydroxide, it is found that the amounts of certain reaction products are definitely dependent upon the normality of the solutions used and also upon the temperature employed. In a recent report, Shaffer and Friedman[1] have shown that the concentration of the sugar is also an important factor in the reaction of the hexose sugar under these conditions.

Since it is conceivable that pentose sugars may be formed as intermediate compounds in reactions involving the decomposition of hexose sugars in alkaline solutions, it becomes of much interest to know whether the products formed in a similar decomposition of the pentoses will show the same general relationship to the experimental conditions used as the hexose sugars do under similar circumstances. To obtain data with reference to this point was the principal objective in these experiments. For our experimental purposes we used the two easily accessible five-carbon atom sugars, *l*-arabinose and d-xylose. A similar study concerning the theoretically possible intermediate trioses has been made in this Laboratory previously.[2]

Experimental

(a) Materials.—All materials used in these experiments were examined for their purity by well-known laboratory methods.

(b) Manipulation. Lactic, Acetic and Formic Acids.—A 100-cc. round-bottomed pyrex flask containing 25 cc. of potassium hydroxide of the desired normality was attached to a mechanical agitator placed in a thermostat. After sufficient time had elapsed for the flask and its contents to come to the desired temperature (25, 50 or 75°), 1.875 g. (0.5*M*) of the crystalline *l*-arabinose or d-xylose was added through a large funnel whose stem had been shortened. Usually ten samples, including different normalities and duplicates, were started within the period of an hour. As in all the previous studies in this series, the agitation of these solutions was continued for forty-eight hours. Owing to the difficulties arising from the deposition of moisture during the preparation of the reacting systems at 75°, it was found more convenient to place the sugar in the flask first and then add the standard alkali solution. The general procedure from this

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[1] Shaffer and Friedman, *J. Biol. Chem.*, 86, 345 (1930).

[2] (a) Evans and Hass, THIS JOURNAL, 48, 2703 (1926); (b) Evans and Cornthwaite, *ibid.*, 50,486 (1928).

point on for the determination of lactic, acetic and formic acids has been described previously. It was found that the difficulties attending the determination of zinc lactate due to the presence of large amounts of gum (probably a mixture of the zinc salts of saccharinic acids) could in some measure be overcome by boiling the aqueous solution with a little norite before removing the insoluble zinc carbonate. Obviously, this also introduces a possible error for zinc lactate.

In the determination of formic acid it was found best to attach a Kjeldahl bulb to the distilling column in order to prevent any of the solution from bumping over into the distillate. The receiver, a 250-cc. distilling flask, was completely immersed in a freezing mixture of salt and ice. A piece of glass tubing was sealed to the end of the condenser, in order that the condenser tube might extend down into the bulb part of the receiver. This was done for the purpose of diminishing, as far as possible, the loss of vapors from the receiver.

The distillations were carried to dryness, after which about 10 cc. of distilled water was added to the dry salt residue and the distillation again carried to dryness. It was found that much better results could be obtained in the formic acid determination by thus distilling the residues to dryness three or four times.

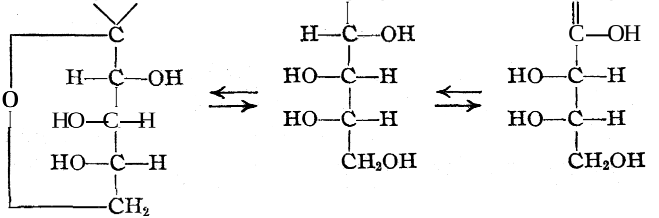
After the distillation was complete, the stem of the Kjeldahl bulb which extended into the flask was rinsed into the salt residue, while the remainder of the bulb and the condenser was rinsed with distilled water into the distillate. The distillate was then carefully transferred to a 100-cc. calibrated flask. After the temperature of the distillate had adjusted itself to that of the room, enough distilled water was added to make a volume of 100 cc.

Pyruvic Aldehyde Osazone.—In this determination, 25 cc. of the standard potassium hydroxide solution was placed in a 100-cc. round-bottomed flask, together with 17.5 cc. of 95% ethyl alcohol and 1.875 g. of the pentose sugars. After being agitated for forty-eight hours at the desired temperature, the pyruvic aldehyde osazone was determined as previously described.

Theoretical Discussion and Summary

When the behavior of I-arabinose and d-xylose in alkaline solutions is examined from the standpoint of their ability to form enediols in the same manner as has been repeatedly discussed for the hexose sugars, then it is possible to predict that the pentose sugars will form certain compounds which are also formed in the alkaline decomposition of the hexose sugars. Nef[3] made an exhaustive study of the behavior of these two pentose sugars in 8 N potassium hydroxide solution, and in an earlier report he gave an account of the behavior of I-arabinose in an alkaline cupric hydroxide system.

***l*-Arabinose 1,2-Enediol.**—The behavior of *l*-arabinose under our experimental conditions is shown in the equations



l-Arabinose *l*-**Arabinose,** aldehyde form *l*-**Arabinose 1,2-enediol**

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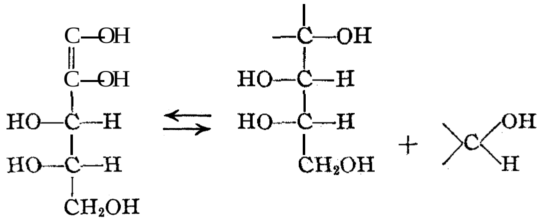
[3] **Nef,** (a) *Ann.*, **376,** 1 (1910); (b) 357,214 (1907).

If the *l*-arabinose 1,2-enediol should undergo cleavage at the double bond, erythrose and formaldehyde would be formed according to the reaction

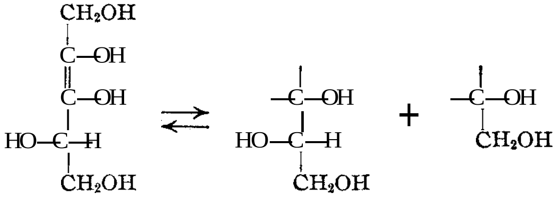


l-Arabinose 1,2-enediol — Erythrose, active form — Formaldehyde, active form

In these experiments the formaldehyde may be regarded as one of the sources of formic acid. Nef[3a] found that 8 N alkaline solutions of glycol aldehyde gave traces only of formic acid and no lactic acid. It has been shown in this Laboratory[4] that alkaline solutions of glycol aldehyde extending over 0.1–10 N give no trace of lactic acid under the experimental conditions which are employed in these experiments. However, such solutions gave rise principally to C_4 saccharins, which must have arisen from the tetroses formed.[5]

Therefore it follows that the lactic acid found in our experiments must have arisen through some other possible decomposition of the pentose sugars than through the intermediate formation of a tetrose sugar. Obviously, the same general structural relations and conclusions are equally true for d-xylose.

***l*-Arabinose 2,3-Enediol.**—As the concentration of the alkali is increased, the pentose sugars should give rise in each case to 2,3-enediols, which in turn may undergo a cleavage at the double bond, thus giving rise to glyceric aldehyde and glycol aldehyde. These changes are shown in the equation



I-Arabinose 2,3-enediol — Glyceric aldehyde active form — Glycol aldehyde active form

(a) Lactic Acid.—In the absence of an oxidizing agent, glyceric aldehyde becomes the source of lactic acid, through the intermediate formation of pyruvic aldehyde. If the alkaline solutions of these pentose sugars contain equilibrated systems,[6] similar to those which have been thought to

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[4] To be published.

[5] *Cf.* Fischer and Landsteiner, *Ber.*, 25,2549 (1892).

[6] *Cf.* Spoehr and Strain, J. *Biol. Chem.*, 85, 365 (1929).

exist in alkaline solutions of the hexose sugars under the same conditions, then it would follow that the quantity of lactic acid formed should increase

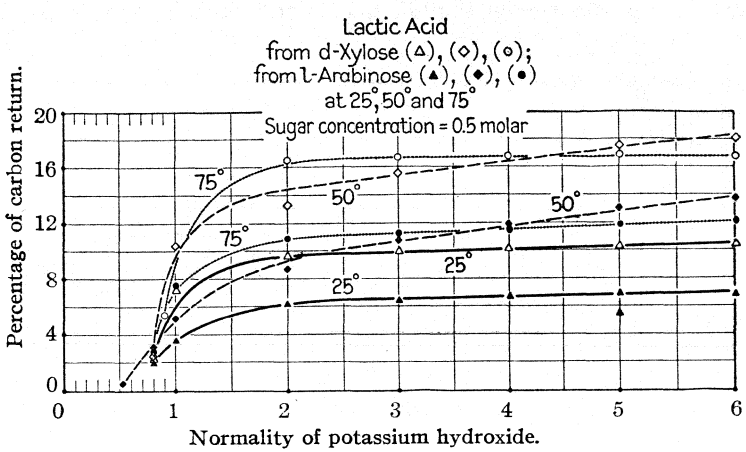

Fig. 1.

with an increase in the alkali normality. That this general relationship holds true may be seen in Fig. 1. Thus we see that the same general temperature relationships are also found to exist in the formation of lactic

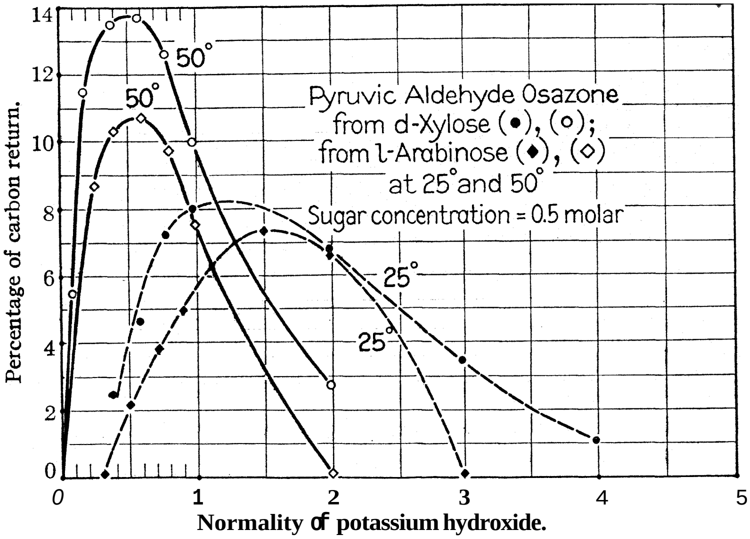

Fig. 2.

acid from the alkaline pentoses as were observed in the solutions of the hexoses. As the temperature rises, it is seen that the rate of formation of lactic acid at 75° becomes less than that at 50°. This same observation has also been made previously with mannose,[7] glucose,[7] fructose[8] and the trioses.[2] Although the cause of this difference has not been systematically investigated, yet this change may be due to an increasing rate of formation

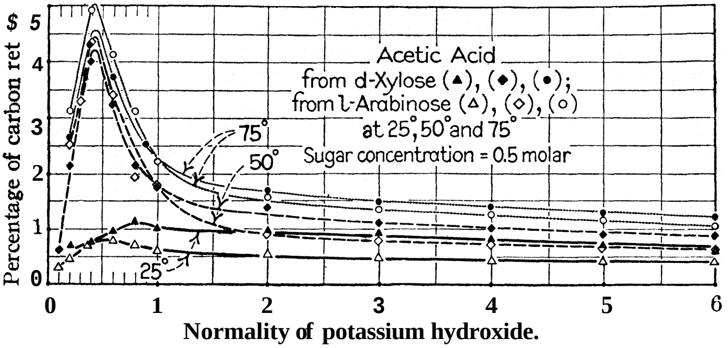

Fig. 3.

of the saccharinic acids arising from an increasing temperature, a condition which obviously would result in a corresponding decrease of the alkali normality of the reacting system due to neutralization. In time this would tend to diminish the pentose 2,3-enediol formation.

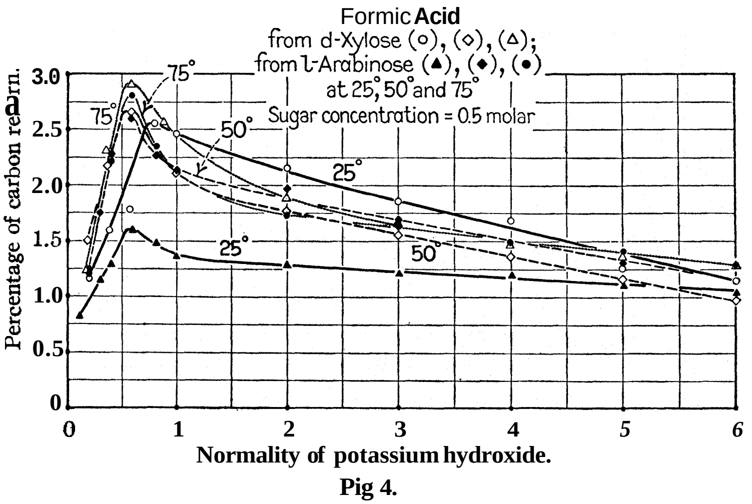

Fig. 4.

(b) **Pyruvic Aldehyde.**—It is generally accepted that pyruvic aldehyde formation is the forerunner of lactic acid in the alkaline decomposition of the sugars. Since this acid was found in these reactions with the pentoses an examination was made for the presence of pyruvic aldehyde.

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[7] Evans and O'Donnell, This Journal, 50, 2550 (1928).

[8] Evans and Hutchman, *ibid.*, 50, 1497 (1928).

Our results are shown in Fig. 2. The temperature and alkali effects are practically the same as those which have been observed in this Laboratory with the trioses,[2] certain hexoses[7,8] and maltose.[9]

(c) Acetic and Formic Acids.—Previously it has been thought that the presence of acetic acid in these reactions might be due to a decomposition of pyruvic aldehyde into acetaldehyde and carbon monoxide, which, in turn, would yield acetic and formic acids, respectively. If this were true, then these acids should also show maximum yields, because the tendency of the pyruvic aldehyde toward a minimum after the maximum, has been thought to be due to the increasing rate of lactic acid formation with the increasing normality of the alkali. That these general considerations are also true in the alkaline decomposition of the pentoses may be seen in Figs. 3 and 4. It is also conceivable that the glycol aldehyde which is formed in the decomposition of the 2,3-pentose enediols as well as the 1,2-triose and 2,3-hexose enediols may also give rise to acetic acid formation.[10]

From the data presented in this report it is clear that any pentoses which might possibly form in the alkaline decomposition of the hexose sugars are to be considered as possible sources of pyruvic aldehyde, lactic, acetic and formic acids.

COLUMBUS, OHIO

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

A MODIFICATION OF THE SKRAUP SYNTHESIS OF QUINOLINE

BY ESSIE WHITE COHN

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The Skraup synthesis is widely used as a method for the preparation of quinoline and its derivatives. The synthesis, when performed in the manner advocated by Skraup, is often accompanied by a violent reaction. In addition, the yields obtained are variable and often low. To overcome the disadvantages of the original Skraup method, various improvements have been published from time to time.

To date the most important of the improvemerits made have been the ferrous sulfate modification of Clarke and Davis,[1] the acetic acid modification of Cohn and Gustavson[2] and a thorium–vanadium oxide method of Darzens, Delaby and Hiron.[3] The ferrous sulfate modification gives a very much better yield than does the original Skraup method. The re-

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[9] Evans and Benoy, THIS JOURNAL, 52,294 (1930).

[10] (a) R. C. Hockett, Master's Thesis, The Ohio State University, 1928; (b) G. P. Hoff, Doctor's Dissertation, 1925; (c) *cf.* Evans, *Chemical Reviews,* 6, *306* (1929).

[1] Clarke and Davis, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1922, Vol. II, p. 79.

[2] Cohn and Gustavson, THIS JOURNAL, 50, 2703 (1928).

[3] Darzens, Delaby and Hiron, Bull. *soc. chim.,* 47,227 (1930).

action, however, is sometimes violent. The acetic acid modification accomplishes a complete removal of all traces of violence. The yields obtained by this method are smaller than those of the ferrous sulfate modification. The modification which has been named the thorium–vanadium oxide modification gives good yields. The violence of reaction has been avoided by adding sulfuric acid in three stages, controlling the temperature at which the reaction mixture is refluxed and by stirring.

Since each of these methods leaves something to be desired from the standpoint of smoothness in the first method, of yield in the second and of convenience in the third, the present paper presents a method which moderates the violence of the reaction and produces yields comparable with those obtained by other methods. This method will be termed a boric acid modification.

Experimental

The boric acid modification of the ferrous sulfate modification method for preparing quinoline may be carried out as follows. The reagents are placed in a liter flask in the order given: 14 g. of ferrous sulfate, **38** g. of aniline, **29.5** g. of mononitrobenzene. Twenty-five grams of boric acid is dissolved in **150** g. of glycerol, heat being used to effect solution of the boric acid. The boric acid–glycerol mixture when cooled is added to the contents in the liter flask and the whole mixed. Finally, **69.8** cc. of **95%** sulfuric acid is added, the contents mixed well, connected with a reflux condenser and heated over a free flame until the boiling point is reached. The mixture in the flask is kept simmering for a period of refluxing from nine to twenty hours, depending upon the yield desired. It is then cooled and diluted with water. The flask is connected with steam distillation apparatus and steam is passed in until the distillate is clear. The contents of the flask are cooled and made alkaline with about **250** cc. of a **60%** sodium hydroxide solution. The sodium hydroxide is added cautiously with frequent cooling of the flask. The contents of the flask are again distilled with steam. The current of steam is discontinued when the distillate is clear. The distillate is dissolved in sulfuric acid **(25.7** cc. of 95% sulfuric acid diluted with an equal volume of water). The mixture is cooled, sodium nitrite added until a drop of the solution causes a starch–potassium iodide spot to turn blue and the material is allowed to stand for about an hour. The contents of the flask are again made alkaline and steam distilled until the distillate is clear. The distillate is extracted with ether, the ether evaporated and the resulting product of quinoline weighed. Comparisons are based on the weight of quinoline obtained at this stage, although further purification is effected by distillation.

The following table shows a comparison of yields obtained by three methods of preparing quinoline for a five-hour period of refluxing. The yields are based on the same quantity of aniline and approximately the same quantities of materials with the exception of ferrous sulfate, acetic acid and boric acid.

Method	Time of heating, hours	Average yield, *g.*
Ferrous sulfate modification...............	5	30
Acetic acid modification..................	5	25
Boric acid modification....................	5	38

Figure 1 shows the yield obtained in the boric acid modification method as the time of refluxing was varied. For a fifteen-hour refluxing, the yield of quinoline is 90% of the theoretical based upon the amount of aniline originally added.

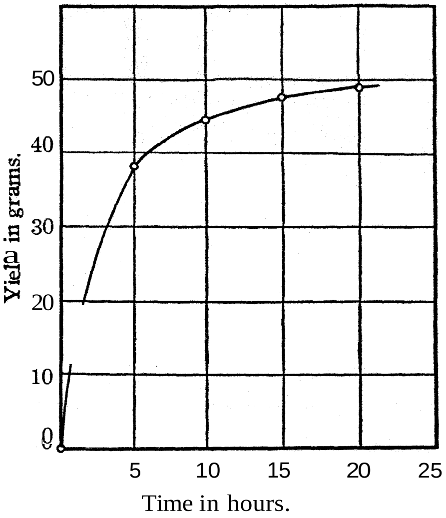

Fig. 1.—Yield of quinoline with time of refluxing.

The theory for the action of boric acid is believed to be similar to that of the acetic acid modification of Cohn and Gustavson,[2] namely, that an intermediate semi-stable glycerol borate is formed which hydrolyzes, gradually liberating glycerol.

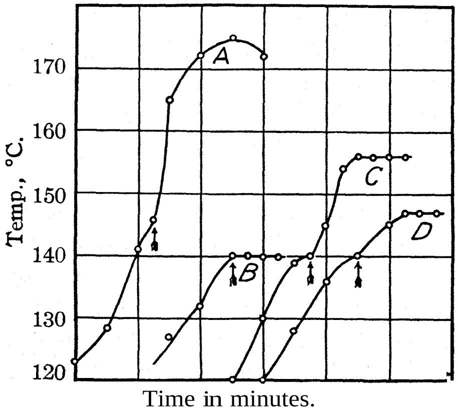

Fig. 2.—Comparative initial rise of temperature with time of heating.

A Measure of the Vigor of the Initial Reaction.—To obtain a more definite measure of the violence of the various reaction mixtures used in the synthesis of quinoline, the rate of rise of temperature under uniform heating conditions was obtained for each. The method used was to place in an 8-inch pyrex test-tube a fixed volume of the mixture to be tested. The tube was placed in an electrically heated vertical tube furnace of small heat capacity constructed for this experiment. The furnace was started in all cases at a temperature of 20° and was heated by a current of 1.80 amperes with constant stirring of the mixture. The increase in temperature with time was noted. Figure 2 shows typical curves obtained. These curves represent in a graphic manner the relative vigor of the reactions encountered in each case. The temperature at which bubbles began to escape is marked with an arrow. This point may not represent the boiling point of the mixture as a whole. Curve **A** represents the temperature–time curve above 120° for the original Skraup mixture. The temperature at which bubbles escape from the solution is approximately 146°. It will be noted that the temperature rise above this point is extremely rapid, reaching within the next minute about 175°. The rapid change in temperature is apparently related to the violence of the reaction. Curve B indicates the entire lack of violence found in the acetic acid modification. In Curve C, representing the curve obtained in the ferrous sulfate modification, the rise of temperature after the evolution of bubbles can be seen to approximate 15° within one-half minute. In Curve D, which represents the data from the boric acid modification, the rise of temperature is approximately one-half of that found in Curve C and, as will be noted by the slopes of the two curves, the rise is more gradual.

Summary

1. It has been found possible to decrease the violence of the reaction of the ferrous sulfate modification of the Skraup quinoline synthesis by the addition of boric acid.

2. The yield of quinoline has been increased by the addition of the boric acid.

3. A comparison of the vigor of the reactions has been obtained.

DENVER, COLORADO

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, THE UPJOHN COMPANY]

THE STEROLS OF ERGOT. II. THE OCCURRENCE OF DIHYDRO-ERGOSTEROL

BY FREDERICK W. HEYL AND ORLO F. SWOAP[1]

RECEIVED JUNE 9, 1930 PUBLISHED SEPTEMBER 5, 1930

Recently[2] we briefly described the preliminary fractionation of "ergosterol" from ergot fat. Crude ergosterol was prepared from an ether solution of the unsaponifiable fraction by precipitation with petroleum ether. We have now studied this ether–petroleum ether filtrate. Originally our expectation was that fungisterol might be found there in such proportion that its isolation would be somewhat more readily accomplished. In this study we have incidentally isolated pure α-dihydro-ergosterol, which was first described by Windaus and Brunken.[3] They report a specific rotation of $-19.3°$, and a melting point of 173–174°. The acetate melts at 180–181° and for $[\alpha]_D$ they found $-21.0°$ Heilbron, Johnstone and Spring[4] report that the melting point of a-dihydro-ergosterol acetate varies from 179–180 to 173°, depending upon the duration of the acetylation process. The rotation, $[a]_{5461}^{21}$, varied from -25.3 to $-30.3°$.

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[1] Holder of the Upjohn Cooperative Fellowship at Kalamazoo College (1929–1930). This paper is based upon the thesis presented by Mr. Swoap to the Faculty of Kalamazoo College, in partial fulfilment of the requirements for the degree of Master of Science.

[2] Hart and Heyl, THIS JOURNAL, 52,2013 (1930).

[3] Windaus and Brunken, Ann., 460,232 (1928).

[4] Heilbron, Johnstone and Spring, J. Chem. *Soc.*, 2248 (1929).

a-Dihydro-ergosterol, isolated from ergot fat, melted at 172.5–175°, gave an acetate melting at 176–177° and for $[\alpha]_D^{26}$ we found − 20.6". The benzoate melted at 153–155° and the color tests agreed with those known for this substance.

This result is what one might expect since Anderson has repeatedly shown that sitosterol is accompanied by dihydrositosterol in corn oil,[5] wheat embryo,[6] and rice bran.[7] Consequently a mixture of very closely related alcohols in various stages of saturation might be anticipated in the unsaponifiable matter of ergot fat.

Experimental

A quantity of petroleum ether-ether filtrates from ergosterol had separated a quantity of crystalline material upon long standing. This was filtered off and lightly washed with petroleum ether. A quantity (74 g.) was fractionally crystallized from ethyl acetate. The top fraction melted at 158.5–160°; intermediate fractions showed a series of melting points of about 121–125°, and the bottom fractions melted below 100°. A further quantity (312 g.) of the crude material was fractionally crystallized in the same way and separated into 33 fractions after an elaborate system of recrystallizations.

Fractions 6, 7 and 8, aggregating about 5 g., showed rotations of —22.5, —22.5 and —19.1°, respectively, and from these, by further elaborate fractional crystallization from alcohol, α-dihydro-ergosterol was isolated. For example, the fractionation of fraction 8 (2.3 g.) yielded the following fractions:

Fraction no.	Weight, g.	M. p., °C.	$[\alpha]_D$
8A	0.45	165–167	−25.0
8B	.14	159–164	−25.4
8C	.24	161–164	−22.66
8D	.08	156–159	−12.4
8E	.15	137–150	− 9.5

Of these, A, B and C were acetylated separately:

Fraction no.	Weight, g.	M. p., °C.	$[\alpha]_D$
Acetate 8A	0.26	171–173	−19.75
8B	.10	169–173	−19.0
8C	.20	167–173	−18.1

8A, 8B and 8C were combined with acetate fraction 7C (m. p. 167–170°; $[\alpha]_D$ −17.0). The acetate was recrystallized several times from ethyl alcohol, when it melted at 176–177°.

Anal. Calcd. for $C_{27}H_{43}OCOCH_3$: C, 81.60; H, 10.87. Found: C, 82.02; H, 10.60.

The above acetate was saponified with 3% methyl alcoholic potash and the recovered alcohol was crystallized three times from methyl alcohol. Pure a-dihydro-ergosterol as leafy needles melting at 172.5–175° and $[\alpha]_D^{26}$ − 20.6 was isolated.

Anal. Calcd. for $C_{27}H_{43}OH$: C, 84.30; H, 11.54. Found: C, 84.52; H, 11.54.

Color Tests of α-Dihydro-ergosterol.—With the Rosenheim trichloro-acetic acid, a

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[5] Anderson, This Journal, **46**, 1450 (1924).

[6] Anderson and Nabenhauer, ***ibid.***, **46**, 1717 (1924).

[7] Nabenhauer and Anderson, ***ibid.***, **48**, 2972 (1926)

completely negative test resulted. With Salkowski test, the chloroform was colorless and the sulfuric acid layer orange-yellow. With the Liebermann-Burchard test the color transitions were as follows: very slight pink, transitory lavender, deep blue, slowly to green.

α-Dihydro-ergosterol Benzoate.—The alcohol (0.1 g.) was dissolved in pyridine (2 cc.) and 2 drops of benzoyl chloride added. The benzoate precipitated and after long standing was filtered off and recrystallized from alcohol. It melted at 153–155°.

Anal. Calcd. for $C_{27}H_{43}OCOC_6H_5$: C, 83.55; H, 9.90. Found: C, 83.10; H, 10.33.

The benzoate gave the same color reactions described above and in addition gave a positive reaction to the Heilbron and Spring[8] modification of the Tortelli–Jaffe reaction.

Reduction to α-Ergostenol.—Three-tenths of a gram of the acetate was reduced with Adams' platinum oxide catalyst as previously described[9] and a top fraction of α-ergostenol acetate melting at 110–111° was obtained. Upon saponification with 3% methyl alcoholic potash, α-ergostenol melting at 133° was obtained.

Summary

From the unsaponifiable fraction of ergot fat, α-dihydro-ergosterol has been isolated. The alcohol itself melted at 172.5–175° and gave $[\alpha]_D^{26}$ −20.6°. The acetate of α-dihydro-ergosterol melted at 176–177° and the benzoate at 153–155°. The color reactions agree exactly with those described by Windaus and Brunken, and by Heilbron and Spring.

KALAMAZOO, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO ORGANIC GERMANIUM DERIVATIVES. III. DIPHENYL GERMANIUM DIHALIDES AND DIPHENYL GERMANIUM IMINE

BY CHARLES A. KRAUS AND CECIL L. BROWN

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I. Introduction

The present is one of a series of papers relating to the chemistry of the typical amphoteric elements. It may be considered that all the elements from the first to the seventh groups inclusive, which have a deficiency of from seven to one electrons with respect to the rare gas type, are amphoteric. The elements that have a deficiency of only one or two electrons are strongly electronegative and their amphoteric tendencies are not marked. On the other hand, those elements that have a deficiency of five, six or seven electrons usually act electropositively and their electronegative characteristics are not pronounced. Amphoteric properties are most marked in the elements of the fourth group, which have a deficiency of four electrons. In the case of carbon, this property is well illustrated by triphenylmethyl. The triphenylmethyl group combines, on the one hand, with negative

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[8] Heilbron and Spring, *Biochem. J.*, 24, 133 (1930).

[9] Hart, Speer and Heyl, THIS JOURNAL, 52, 2017 (1930).

elements or groups to form compounds that, under certain conditions, exhibit electrolytic properties. On the other hand, the same group combines with the alkali metals to form relatively stable compounds which are typical salts and in which the triphenylmethyl group acts as anion. Triphenylmethyl also exists in the neutral state. In other words, triphenylmethyl exists in three states of oxidation: as a positive group, as a neutral group, and as a negative ion.

While in certain respects carbon is the ideal amphoteric element, in other respects other elements of the fourth group exhibit amphoteric properties more commonly. Previous investigations have shown that the tertiary organic derivatives of tin, whether alkyl or aryl, are uniformly amphoteric.[1] And not only may we obtain univalent amphoteric groups in the case of tin; we may also obtain divalent groups. Thus Kraus and Greer[2] have shown that dimethyl tin acts electropositively toward the halogens, while it also combines with sodium to form a divalent anion. Similar properties have been found in the case of the diphenyl tin group.''

Our knowledge of corresponding groups of germanium and silicon is very limited. In general, the study of these groups is rendered difficult because of the ease with which their halogen derivatives are ammonolyzed. Kraus and Foster,[3] however, have investigated the triphenyl germanium group. Investigations relating to silicon, germanium and boron have been under way in this Laboratory for some years and the results will be published from time to time. The present investigation is specifically directed toward the isolation of diphenyl germanium and the preparation and properties of some of its derivatives. It was found that the diphenyl germanium group lends itself to study less readily than do corresponding derivatives of tin. Furthermore, our knowledge of organic germanium derivatives generally is very limited so that it was found necessary to study many problems relating to source materials.

Among the earlier investigations relating to phenyl germanium derivatives may be mentioned those of Morgan and Drew,[4] who prepared tetraphenyl germanium and some other phenyl derivatives, and Tabern, Orndorff and Dennis: who prepared tetraphenyl germanium as well as other quaternary alkyl and aryl germanium compounds. The work of Kraus and Foster, in this connection, has already been referred to.

In the present investigation, diphenyl germanium dihalides were first prepared and characterized. The action of ammonia and ethylamine on diphenyl germanium dihalides was also studied and, finally, diphenyl

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[1] (a) Kraus and Sessions, THIS JOURNAL, 47, 2361 (1925); (b) Kraus and Bullard, *ibid.*, 48, 2131 (1926); (c) Chambers and Scherer, *ibid.*, 48, 1054 (1926).

[2] Kraus and Greer, *ibid.*, 47, 2568 (1925).

[3] Kraus and Foster, *ibid.*, 49, 457 (1927).

[4] Morgan and Drew, *J. Chem. Soc.*, 125, 1261 (1924).

[5] Tabern, Orndorff and Dennis, THIS JOURNAL, 49, 2512 (1927).

germanium was prepared in the free condition. Its physical properties and chemical reactions were investigated; disodium diphenyl germanide was prepared and octaphenyl germanopropane was synthesized. The two last-named compounds will be described in a succeeding paper.

11. Diphenyl Germanium Dihalides

Method of **Preparation.—Tetraphenyl** germanium served as source material for the preparation of the dihalides. This compound was prepared according to the method of Kraus and Foster[3] and preparative details need not be described here. It was recrystallized from trichloro-ethylene and melted at 230–231° (corr.).

According to Kraus and Foster, tetraphenyl germanium is brominated with considerable difficulty, although they were able to prepare the monobromide by boiling a mixture of the compound with the theoretical amount of bromine in carbon tetrachloride for a considerable period of time. The second phenyl group is substituted even less readily than the first. Preliminary experiments confirmed the observations of Kraus and Foster, but on further study it was found that the rate of bromination is greatly dependent upon the concentration of bromine. On boiling a mixture of **37** g. of tetraphenyl germanium and 15 cc. of bromine in 70 cc. of carbon tetrachloride for ten hours, a fairly satisfactory yield of diphenyl germanium dibromide was obtained. The product, however, was impure, containing some of the monobromide and a smaller proportion of the tribromide. Since completing the present investigation, Tabern, Orndorff and Dennis[5] have shown that tetraphenyl germanium is more readily brominated in ethylene dibromide.

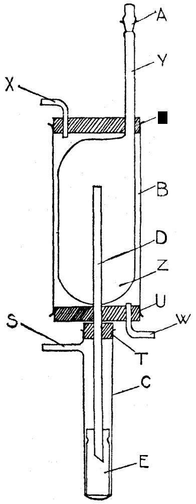

Fig. 1.

In brominating tetraphenyl germanium, a mixture of bromides is in general obtained and separation becomes necessary. An attempt to fractionally distil the bromides did not prove particularly successful. Diphenyl germanium dibromide is not very volatile at 100°, even at a pressure as low as 0.005 mm. Accordingly, it was found more convenient to convert the mixture of bromides to chlorides. The original mixture was separated from residual impurities by vacuum distillation at 150°. The distillate was placed in an evaporating dish, a little alcohol was added and then strong ammonium hydroxide to complete the hydrolysis. The mixture was boiled for some time, in which process most of the phenyl bromide was carried off with the steam. On cooling, a mixture of oxides solidified. The solid mass was separated from the aqueous solution, washed and dried. These oxides were then converted to chlorides by heating with concentrated hydrochloric acid. The desired product settled to the bottom as a heavy liquid which was extracted with benzene. After removal of most of the solvent, the product was introduced into a special still and fractionated under reduced pressure.

The distillation apparatus consisted of a pyrex tube **Z**, which was provided with a steam jacket B, the tubes X and W serving as inlet and outlet tubes, respectively. The liquid to be distilled was introduced through the tube Y, which was provided with a ground stopper **A.** The vapors from the liquid passed down through the re-entrant tube D. The condensate was collected in a small bottle E, which was contained in a wide test-tube C. This tube was attached to the distillation apparatus by means of a rubber stopper T. The side tube S, attached to the test-tube, was connected to a vacuum pump, a McLeod gage being connected in the exhaust line.

Diphenyl germanium dichloride distils readily at 100° under a pressure of 0.005 mm. The yield of dichloride, based on the weight of original tetraphenyl germanium used, ranged from 40 to 60%. The purity was tested by analysis.

Diphenyl Germanium Dichloride.—Diphenyl germanium dichloride is a colorless liquid. According to Sherman[6] it freezes at lower temperatures and melts at 9°. Its density is greater than that of water. It is readily soluble in ordinary organic solvents. It is slightly hydrolyzed in moist air, more rapidly in water and alcohol, and still more rapidly in alkaline solution.

The compound was analyzed for both germanium and chlorine. For the halogen determinations, from 0.2- to 0.3-g. samples were treated with dilute ammonium hydroxide, the mixture being stirred until the oxide was reduced to fine powder. It was then thrown onto a filter and the oxide was thoroughly washed. The ammoniacal filtrate was acidified with nitric acid and the chlorine was precipitated with silver nitrate and weighed as silver chloride.

Anal. Subs., 0.1836, 0.2460, 0.2721: AgCl, 0.1758, 0.2375, 0.2639. Calcd. for $(C_6H_5)_2GeCl_2$: Cl, 23.83. Found: Cl, 23.68, 23.88, 23.99, mean, 23.85.

The germanium was determined by a modification of the Krause method.[7] Samples of the dichloride were introduced into a pyrex tube (22 × 2.5 cm.) which had been heated to constant weight. About 5 cc. of fuming sulfuric acid was added with shaking, followed by 5 cc. of fuming nitric acid, which was added slowly. The mixture was then boiled for about twenty hours. Whenever the nitric acid content became low, as was indicated by the color of the fumes, more was added to the cooled solution. When oxidation was thought to be complete, the acids were boiled off. If the organic material was incompletely oxidized, a black deposit was formed on the walls of the tube as the residue dried up. In that case, more nitric acid was added and the sample was boiled for some hours longer. Kemoval of the acids was facilitated by drawing a gentle current of air through a glass tube, the end of which was located midway along the axis of the analysis tube. Certain of the phenyl germanium derivatives are oxidized with extreme difficulty. The method here described is effective in all cases provided that the process is continued for a sufficient length of time. After removing the acid, the oxide was ignited at a dull red heat until constant weight was reached.

Anal. Subs., 0.3068, 0.3161, 0.1940: GeO_2, 0.1085, 0.1115, 0.0677. Calcd. for $(C_6H_5)_2GeCl_2$: Ge, 24.39. Pound: Ge, 24.54, 24.48, 24.22; mean, 24.40.

Diphenyl Germanium Dibromide.—Diphenyl germanium dichloride of known purity was hydrolyzed and the resulting oxide was converted to the dibromide by heating with strong hydrobromic acid. The oily liquid was extracted with benzene, the solvent was removed and the dibromide distilled in *vacuo* at 120° under a pressure of 0.007 mm. The properties of the dibromide correspond closely to those of the dichloride except that it is markedly less volatile.

The bromine content of the compound was determined by hydrolyzing a known sample of the compound with a weak solution of sodium hydroxide, separating the sodium bromide solution from the solid diphenyl germanium dibromide and precipitating the bromine as silver bromide. The germanium content was determined by the method already described in connection with the analysis of the dichloride.

Anal. Subs., 0.3542, 0.4068: AgBr, 0.3434, 0.3940. Calcd. for $(C_6H_5)_2GeBr_2$: Br, 41.35. Pound: Br, 41.26, 41.22; mean, 41.24. Subs., 0.2275, 0.2117; GeO_2, 0.0620, 0.0572. Calcd.: Ge, 18.78. Pound: Ge, 18.91, 18.75; mean, 18.83.

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[6] Unpublished observations by C. S. Sherman in this Laboratory.

[7] Krause, *Ber.*, 55, 896 (1922); Kraus and Bullard, THIS JOURNAL, 51, 3606 (1929).

Diphenyl Germanium Difluoride.—The difluoride was prepared by treating diphenyl germanium oxide (resulting from hydrolysis of the chloride) with hydrofluoric acid. Most of the excess acid was evaporated and the difluoride was extracted with benzene. After removal of the solvent, the fluoride was distilled in *vacuo* at 100° at a pressure of 0.007 mm. The germanium content of the difluoride was determined by the method already described.

Anal. Subs., 0.1490, 0.1471: GeO_2, 0.0585, 0.0576. Calcd. for $(C_6H_5)_2GeF_2$: Ge, 27.43. Found: Ge, 27.25, 27.18; mean, 27.22.

The fluorine was determined by the method of Starck.[8] The difluoride was hydrolyzed with sodium hydroxide and the solution separated from the resulting oxide by filtration. To the filtrate was added sixteen drops of concentrated hydrochloric acid, the solution being warmed to 40°. Methyl orange was then added and the solution acidified with nitric acid, allowing three drops in excess. Ten drops of glacial acetic acid and 25 cc. of a filtered solution (10%) of lead acetate containing 1% of acetic acid were added under stirring. Fluorine was precipitated as lead chlorofluoride. The precipitate was allowed to stand overnight, when it was filtered and weighed in a Gooch crucible.

Anal. Subs., 0.2983, 0.2944: PbClF, 0.5273, 0.5731. Calcd. for $(C_6H_5)_2GeF_2$: F, 14.36. Pound: F, 13.93, 14.04; mean, 13.98.

Diphenyl germanium difluoride is a colorless liquid which is decidedly more volatile than the corresponding chloride. Of the three dihalides studied, it is the most sensitive toward moisture. On standing in the air but a short time, a film of oxide is formed on the surface of the liquid. This layer protects the remainder of the liquid against further hydrolysis. It is readily soluble in the common organic solvents.

III. Diphenyl Germanium Oxide

Morgan and Drew[4] have prepared diphenyl germanium oxide by hydrolyzing mixtures of bromides containing dibromide. From this mixture they separated a partially dehydrated hydroxide and a complex oxide that melted at 149 and 218°, respectively. It seemed worth while to examine the oxide obtained on hydrolyzing a pure dihalide. Accordingly, a quantity of the dichloride was hydrolyzed by the method already described. After drying, it was analyzed for germanium.

Anal. Subs., 0.1121, 0.1709: GeO_2, 0.0483, 0.0735. Calcd. for $(C_6H_5)_2GeO$: Ge, 29.92. Found: Ge, 29.90, 29.85; mean, 29.88.

Properties.—The oxide is a white powder which is practically insoluble in organic liquids. Of various samples tested, none was found to have a definite melting point. By extracting with boiling benzene, a minute quantity of oxide was obtained which melted between 133 and 150". By means of boiling alcohol, small quantities were obtained that melted between 140 and 185° and 149 and 300°. The variation of the melting point indicates that, when the dihalides are hydrolyzed, a mixture of complex oxides is produced. It is doubtful whether the simple oxide $(C_6H_5)_2GeO$ can be obtained. A similar mixture of oxides is obtained by hydrolysis of diphenyl germanium imine.

IV. Action of Ammonia on Diphenyl Germanium Dichloride

Kraus and Wooster[9] have shown that triphenyl germanium halides are ammonolyzed by potassium amide in liquid ammonia. It was anticipated that the diphenyl germanium dihalides would be ammonolyzed by liquid ammonia. In preliminary ex-

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[8] Starck, Z. *anorg. Chem.*, *70*, 173 (1911); Hawley, *Ind. Eng. Chem.*, *18*, 573 (1926).

[9] Kraus and Wooster, THIS JOURNAL, 52, 372 (1930).

periments, weighed samples of diphenyl germanium dichloride were sealed in fragile glass capsules which were introduced into one leg of a weighed two-legged reaction tube. This tube was provided with a stopcock through which it was evacuated prior to weighing, and through which ammonia could be introduced as desired. After evacuation, the bulb was broken, the tube was immersed in boiling ammonia and ammonia was condensed upon the dichloride. The reaction mixture was allowed to stand for several hours, after which the solvent was allowed to evaporate. The tube was then again exhausted and weighed. The increase in weight of the tube gave approximately the amount of ammonia added on ammonolysis. The results were as follows: wt. of $(C_6H_5)_2GeCl_2$, 0.2269, 0.2460, 0.2810; gain in wt. as NH_3, 0.0375, 0.0429, 0.0483; moles of NH_3 per mole of dichloride, 2.90, 3.05, 3.00; mean, 2.98. These data indicate that ammonolysis occurs according to the equation

$$(C_6H_5)_2GeCl_2 + 3NH_3 = (C_6H_5)_2GeNH + 2NH_4Cl \qquad (1)$$

In order to separate the organic material from the ammonium chloride, dry benzene was condensed on the product of reaction and the solution was decanted into the second leg of the reaction tube. By repeated distillation and decantation, complete separation of the ammonium chloride was effected. Most of the benzene was then removed by means of an aspirator pump and the last traces by means of a high vacuum pump. Dry nitrogen was introduced and the two legs were separated by sealing off the connecting tube with a blowpipe. The ammonium chloride left behind in the first leg of the reaction tube was analyzed for chlorine. The tube containing the salt was opened, the material was dissolved in water and the halogen determined as silver chloride in the usual way. The results follow, the percentages of chlorine being based on the weight of diphenyl germanium dichloride originally taken.

Anal. Subs., 0.2269, 0.2460, 0.2810: AgCl, 0.2202, 0.2375, 0.2371. Calcd. for $(C_6H_5)_2GeCl_2$: Cl, 23.83. Found: Cl, 24.00, 23.88, 24.04; mean, 23.94.

These results show that the ammonolysis of the dichloride was complete and in accord with Equation 1. Since the weight of the original products of the reaction indicated that three moles of ammonia were involved, the third molecule must have been combined with germanium as an imine group.

Diphenyl Germanium Imine.—The leg containing the soluble product of the reaction was evacuated and freshly distilled water was introduced. A white deposit gradually replaced the colorless viscous liquid in the tube. After standing for twenty-four hours, the stopcock of the tube was connected with a condenser and the liquid contents were distilled and collected in a flask. The distillate was titrated against standard acid.

Anal. $(C_6H_5)_2GeCl_2$, 0.2460, 0.2810: calcd. wt. of imine, 0.1998, 0.2282: cc. of 0.03043 N HCl used, 27.6, 30.7; N, 0.01176, 0.01309. Calcd. for $(C_6H_5)_2GeNH$: N, 5.80. Found: N, 5.89, 5.73; mean, 5.81.

The analyses show that one mole of ammonia is formed on hydrolysis of the imine. The white solid resulting on the hydrolysis of the imine was shown by analysis to be diphenyl germanium oxide.

Anal. Subs., 0.1709, 0.1121: GeO_2, 0.0735, 0.0483. Calcd. for $(C_6H_5)_2GeO$: Ge, 29.92. Found: Ge, 29.85, 29.90; mean, 29.88.

The imine is a colorless liquid which is extremely viscous at ordinary temperatures but becomes markedly more fluid at higher temperatures. It is readily soluble in ordinary organic solvents and is hydrolyzed with extreme ease.

Summary

Diphenyl germanium dibromide was prepared by the direct bromination of tetraphenyl germanium in boiling carbon tetrachloride. The mixture of

bromides so obtained was converted to oxides and in turn converted to the corresponding chlorides. The dichloride was obtained from this mixture by fractional distillation. Pure dibromide and difluoride were prepared by converting pure dichloride to its oxide and treating with hydrobromic or hydrofluoric acid.

The three dihalides are liquids at ordinary temperatures and are readily soluble in the common organic solvents. They may be distilled under pressures below 0.01 mm. at temperatures between 100 and 150". The fluoride is markedly sensitive to moisture.

Diphenyl germanium imine was prepared by the action of liquid ammonia on diphenyl germanium dichloride. It is a highly viscous liquid at ordinary temperatures. It is readily soluble in the common organic solvents and is hydrolyzed with extreme ease.

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, CASE SCHOOL OF APPLIED SCIENCE]

QUINAZOLINES. I. THE INTERACTION OF 2,4-DICHLOROQUINAZOLINE WITH SODIUM ALCOHOLATES AND SODIUM PHENATES WITH THE REPLACEMENT OF ONE HALOGEN TO FORM HALOGEN-OXYGEN ETHERS

BY N. A. LANGE, W. E. ROUSH AND H. J. ASBECK

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Since evodiamine and rutaecarpine, the alkaloids of *Evodia rutaecarpa*, have been shown to be derivatives of quinazolone[1] and since the quaternary salts of a few quinazolines have been found to have a lowering effect on the blood pressure,[2] it appears likely that other compounds of the quinazoline group might possess some desirable medicinal properties. It was during the course of a research now in progress in this Laboratory, the purpose of which was the preparation of a series of quinazoline derivatives for subsequent pharmacological testing,[3] that several anomalous compounds were obtained and a further investigation of these compounds was made because the quinazolines have an intrinsic interest of their own.

When 2,4-dichloroquinazoline (I) in alcohol is treated with sodium ethylate both halogens are replaced by ethoxy groups with the formation of 2,4-diethoxyquinazoline (V).[4] In attempting to prepare a similar ether of quinazoline with the phenolate of resorcinol in alcohol, several compounds were isolated from the reaction product which were found to differ from the expected ether. When phenol was substituted for resorcinol, it

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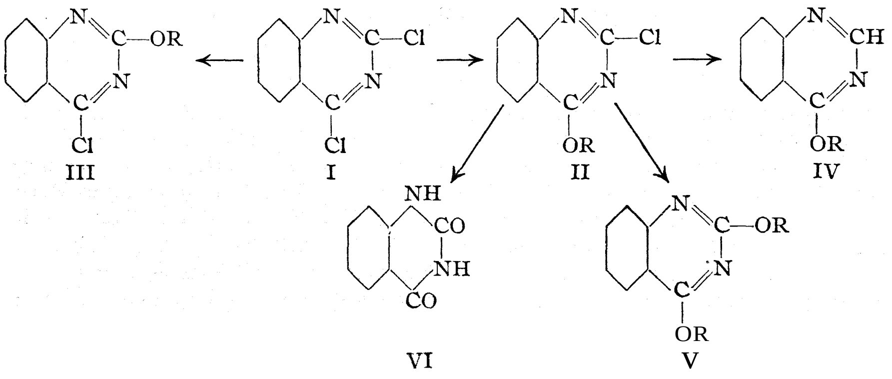
[1] Asahina, Manske and Robinson, J. Chem. *Soc.*, 129, 1708 (1927).

[2] Gabriel and Colman, German Patent 161,401.

[3] The writers are indebted to Professor Marston Taylor Rogert for his suggestion that members of this group of compounds be prepared with this idea in mind.

[4] Aht, J. *prakt. Chem.*, [2] 39, 149 (1889).

was found that one of the reaction products was identical with one obtained when resorcinol was used. On further investigation by chemical analysis, molecular weight determination and chemical properties, the compound was found to be the monochloro-ethoxy derivative of quinazoline (II or III). That a compound with the formula II or III is formed is also shown by the fact that when it is treated with sodium ethylate in ethyl alcohol it yields the diethoxy derivative of quinazoline mentioned above. From this it is evident that one of the two chlorine atoms in dichloroquinazoline is more labile than the other. To establish the position of the unreacted halogen and thus decide whether the structural formula for the compound is best expressed by II or by III, an attempt was made to hydrolyze off the remaining chlorine atom by gently heating the chloro-ethoxy derivative with water. These attempts were not successful as either no hydrolysis took place after a short time or after continued heating both the chlorine atom and the ethoxy group were removed yielding benzoylene urea. The replacement of the halogen by hydrogen by treatment of the Grignard reagent with water was not successful, inasmuch as it was found impossible to bring about the formation of an RMgCl compound with the chloro-ethoxyquinazoline and magnesium. Nearly all of the original chloro-ethoxy derivative was recovered unchanged when the attempted reduction was carried out with (a) sodium amalgam and ether saturated with water, (b) sodium and ethyl alcohol, (c) sodium and ether saturated with water, (d) sodium and amyl alcohol, or (e) zinc, sodium hydroxide and ethyl alcohol; however, when reduced with (f) sodium and methyl alcohol in ether or (g) with zinc and acetic acid in ethyl alcohol, it yielded a product which was found to be identical with the 4-ethoxyquinazoline (IV) previously prepared by Bogert and May.[5] From this it is evident that the structure of the chloro-ethoxy derivative is best expressed by formula II and that the chlorine atom on postion 4 is more reactive than



In compound II, $R = CH_3, C_2H_5, C_6H_5$ or $m\text{-}C_6H_4OH$.

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[5] Bogert and May, THIS JOURNAL, 31,510 (1909).

the chlorine atom on position 2; that groups attached to carbon atom 4 are more labile than those on carbon atom 2 has been observed previously in the case of 4-methoxyquinazoline, which is easily hydrolyzed to 4-quinazolone, whereas 2-methoxyquinazoline required heating with concentrated hydrochloric acid in a sealed tube at 110–120° for one and one-half hours for a similar removal of the alkoxy group[6] and also in the greater ease with which the halogen is removed by hydrolysis from 4-chloroquinazoline as compared with the removal of halogen from 2-chloroquinazoline.[6]

In a similar manner it was found that it is possible to obtain the monochloromethoxyquinazoline. The monochloro-alkoxy derivatives are fairly soluble in petroleum ether; when the original reaction mixture in their preparation is recrystallized from this solvent, varying amounts of an insoluble by-product are obtained which consists almost entirely of the analogous monochlorophenoxy derivative and by varying the amount of phenol used in the reaction the yield of the chlorophenoxy derivative can be increased at the expense of the chloro-alkoxy derivative.

The reduction product of the chloromethoxy derivative was a light yellow oil with a pleasant odor, which did not crystallize on standing for a week in an ice box; whether it would have crystallized on longer standing is not known. However, the oil had characteristics which were the same as those given by Bogert and May[6] for 4-methoxyquinazoline prepared from 4-chloroquinazoline. When the chloromethoxy derivative is treated with sodium methylate in methyl alcohol it gives 2,4-dimethoxyquinazoline.[4]

These reactions for the replacement of but one of the two halogens by means of the presence of phenol appear to offer interesting possibilities in the case of quinazolines for the synthesis of mixed ethers and other similar compounds. Preliminary experiments have shown that this is possible and it is hoped to present these results in a later communication. The possibility of using phenol to repress the activity of the less reactive of two halogens in other types of compounds is also suggested.

Experimental Part

Preparation of 2,4-Dichloroquinazoline, $\overline{\mathrm{N{=}CClC_6H_4N{=}C}}\mathrm{Cl}$ (I).[6,7]—In an acetylating flask were placed 15 g. of benzoylene urea (2,4-diketotetrahydroquinazoline),[8] 40 g. of phosphorus pentachloride and 20 cc. of phosphorus oxychloride and the mixture was refluxed on an oil-bath at 125° for about four hours. The clear brown liquid which results was poured slowly with stirring into 600 cc. of finely crushed ice. The precipitated dichloroquinazoline was immediately filtered off on a Büchner funnel, holding the remaining ice back in the beaker with a stirring rod. The precipitate was thoroughly pressed on the funnel, the aqueous filtrate was discarded and the residue dissolved in

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[6] Gabriel and Stelzner, *Ber.*, 29, 1300 (1896); Gabriel and Colman, *ibid.*, 38, 3559 (1905).

[7] Bogert and Scatchard, THIS JOURNAL, 41, 2061 (1919).

[8] Bogert and Scatchard, *ibid.*, 38, 1612 (1916).

about 500 cc. of ether, using 50-cc. portions of ether at a time and filtering through the same funnel; a small amount of insoluble material remained and was discarded. The combined ether solutions were washed in a separatory funnel, first with dilute aqueous sodium carbonate and then with water. After drying the ether solution overnight with calcium chloride, the ether was removed by distillation from a water-bath, suction being applied at the end of the distillation to remove the last traces of ether. This product (12.4 g.) which remained in the distillation flask was slightly yellow but was found to be sufficiently pure for the syntheses described below. To obtain a very pure product it was dissolved in the minimum amount of boiling toluene, filtered hot, cooled, the crystals filtered with suction and washed with petroleum ether, in which it is insoluble; using the same quantities as above about 6 g. of recrystallized, colorless material was obtained; a further small amount was obtained by adding petroleum ether to the mother liquor; m. p. 120°. The compound must be used shortly after preparation as it gradually decomposes even when protected in a desiccator.

Preparation **of 2-Chloro-4-ethoxyquinazoline,** $\overline{\mathrm{N{=}COC_2H_5C_6H_4N{=}C}}\mathrm{Cl}$ (II).—To 50 cc. of absolute ethyl alcohol in a small flask was added 0.7 g. of sodium, keeping the solution cool; when all of the sodium had reacted, 1.4 g. of phenol was added and then 3 g. of dichloroquinazoline slowly with stirring. The mixture was heated just to boiling and allowed to stand at room temperature overnight; it was then poured into 500 cc. of cold water, where it coagulated in fifteen to twenty minutes; the precipitate was filtered with suction, pressed thoroughly on the filter and recrystallized from petroleum ether, yielding 2.3 g. of colorless crystals; m. p. 92° (corr.). It is readily soluble in benzene, ether, carbon tetrachloride or acetone, fairly soluble in petroleum ether or alcohol, crystallizing well from the latter, and insoluble in water. When subjected to steam distillation a part of the compound volatilized into the distillate; the balance because of hydrolysis to benzoylene urea remained as a non-volatile residue. To determine the best proportions of sodium and phenol, the preparation was carried out as above in 50 cc. of alcohol with 2.5-g. portions of dichloroquinazoline; 0.5 g. of sodium and 2 g. of phenol gave 1 g. of product; 0.5 g. of sodium and 1 g. of phenol gave 2.5 g. of product; 1 g. of sodium and 4 g. of phenol gave 0.8 g. of product and 2.4 g. of chlorophenoxyquinazoline, which is insoluble in petroleum ether and which is described below; 0.5 g. of sodium and 4 g. of phenol gave 0.4 g. of product and 2.1 g. of chlorophenoxyquinazoline. Molecular weight determinations by depression of the freezing point were made with naphthalene as the solvent; the values of 227 and 229 were obtained; the calculated value is 208.5.

Anal. Calcd. for $C_{10}H_9ON_2Cl$: C, 57.55; H, 4.35; N, 13.4; Cl, 17.0. Found: C, 58.01; H, 4.40; N, 13.5; Cl, 17.1.

Preparation **of 2-Chloro-4-methoxyquinazoline,** $\overline{\mathrm{N{=}COCH_3C_6H_4N{=}C}}\mathrm{Cl}$ (II).—This compound was prepared in a methyl alcohol solution in a manner similar to the preparation of the analogous chloro-ethoxy derivative as described above; 2.5 g. of product after recrystallization from petroleum ether was obtained from 0.7 g. of sodium, 50 cc. of methyl alcohol, 1.4 g. of phenol and 3 g. of dichloroquinazoline; it forms colorless crystals from petroleum ether or alcohol; m. p. 99–100° (corr.). It is readily soluble in benzene, ether, carbon tetrachloride or acetone, fairly soluble in petroleum ether, methyl alcohol or ethyl alcohol, and insoluble in water; it is volatile with steam but with partial decomposition into the non-volatile benzoylene urea. A molecular weight determination by the Rast method[9] using camphor for the solvent gave a value of 191; the calculated molecular weight is 194.5.

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[9] Rast, *Ber.*, 55, 1051, 3727 (1922).

Anal. Calcd. for $C_9H_7ON_2Cl$: C, 55.52; H, 3.63; Cl, 18.2. Found: C, 56.28; H, 3.79; Cl, 18.4.

Preparation of **2-Chloro-4-phenoxyquinazoline,** $\overline{N=COC_6H_5C_6H_4N=C}Cl$ **(II).**—This compound was obtained by allowing 0.95 g. of sodium to react completely with an excess of molten phenol; then 8 g. of powdered dichloroquinazoline was mixed with the solid phenol–sodium phenate, which gradually liquefied during the mixing; after standing overnight the reaction mixture was poured into 700 cc. of cold water, when a viscous oil separated; this oil solidified and became granular after the aqueous solution was made slightly alkaline with sodium hydroxide; the solid residue was removed by filtration, washed with water and recrystallized from alcohol; 4.5 g. of colorless crystals was obtained; 2.1 g. of this compound was also obtained from the interaction of 0.5 g. of sodium, 4 g. of phenol and 2.5 g. of dichloroquinazoline in 50 cc. of ethyl alcohol, as described under the preparation of the chloro-ethoxy derivative. The compound is fairly soluble in ethyl alcohol, methyl alcohol, acetone, benzene or ethyl acetate, slightly soluble in ether or chloroform, insoluble in petroleum ether or water; m. p. 121° (corr.).

Anal. Calcd. for $C_{14}H_9ON_2Cl$: Cl, 13.8. Found: Cl, 13.9.

Preparation of **2-Chloro-4-resorcinoxyquinazoline,** $\overline{N=C(OC_6H_4OH)C_6H_4N=C}Cl$ **(II).**—Fifty cc. of absolute ethyl alcohol was treated with 2.5 g. of sodium; after all of the sodium had reacted, 16 g. of resorcinol was added and then 9 g. of dichloroquinazoline was added slowly in small portions during three hours; after standing overnight, the brown colored solution was poured into one liter of water, the mixture made neutral to litmus, the precipitate allowed to coagulate, filtered, washed with water and dried on a suction filter. The air-dried material (9.5 g.) was extracted with boiling petroleum ether, which removed 2.5 g. of chloro-ethoxyquinazoline; the residue of 7 g. was almost completely soluble in boiling alcohol, from which colorless crystals of 2-chloro-4-resorcinoxyquinazoline separated on cooling; m. p. 171–172° (corr.). The solubilities of this compound are like those of the corresponding chlorophenoxy derivative described above.

Anal. Calcd. for $C_{14}H_9O_2N_2Cl$: C, 61.65; H, 3.33. Found: C, 61.78; H, 3.46.

Preparation of **2,4-Diethoxyquinazoline (V).**—Thirty cc. of absolute ethyl alcohol was treated with 0.3 g. of sodium; after all of the sodium had reacted, 2 g. of chloroethoxyquinazoline was added; the solution was warmed gently for five to ten minutes and allowed to stand at room temperature overnight, when about 0.5 g. of sodium chloride separated and was removed by filtration. The filtrate was treated with water, which precipitated 1.8 g. of diethoxyquinazoline; after filtering and drying, it was recrystallized from alcohol, yielding colorless crystals; m. p. 55° (corr.). Although this melting point is 4° higher than that of the diethoxyquinazoline as reported by Bogert and May,[5] there is no doubt as to the identity of the two products, since a sample of the material obtained by their method of preparation also showed a melting point of 55° (corr.) and when the two preparations were mixed the melting point remained unchanged; examination of the two products under a polarizing microscope showed the same angle of extinction in each case.

Anal. Calcd. for $C_{12}H_{14}O_2N_2$: C, 66.02; H, 6.47. Found: C, 66.33; H, 6.62.

Preparation of **2,4-Dimethoxyquinazoline (V).**—This compound was prepared by the interaction of chloromethoxyquinazoline and sodium methylate in methyl alcohol in the same manner as the diethoxy derivative described above. Three grams of chloromethoxyquinazoline and 0.4 g. of sodium in 30 cc. of absolute methyl alcohol gave about 0.9 g. of sodium chloride and 2.7 g. of the dimethoxy derivative, which was recrystallized from alcohol; m. p. 75° (corr.); Bogert and Scatchard[7,8] reported a melting point of 74° for dimethoxyquinazoline but a sample prepared by their method when carefully purified was found to melt at 75°; an examination under a polarizing microscope and a mixed melting point determination of the two products proved their identity.

Anal. Calcd. for $C_{10}H_{10}O_2N_2$: C, 63.12; H, 5.30. Found: C, 63.25; H. 5.38.

Preparation of **4-Ethoxyquinazoline** (IV).—To 6 g. of chloro-ethoxyquinazoline (1 mol) dissolved in 50 cc. of absolute ether were added 0.67 g. of sodium (1 mol) in small pieces and then 0.93 g. methyl alcohol (1 mol); the sodium gradually reacted with the alcohol and after three days at room temperature the sodium chloride was removed by filtration, the ether removed from the filtrate by distillation from a water-bath, suction being applied at the end of the distillation; the light yellow oil which remained was poured on a watch glass and partly solidified on standing for a week in an ice box; the colorless crystals (1 g.) were filtered with suction, pressed between filter paper to remove adhering oil and were recrystallized with much difficulty from alcohol; m. p. 45–48". A better yield of the same product was obtained when 3.6 g. of chloro-ethoxyquinazoline was dissolved in 150 cc. of alcohol, 15 g. of zinc dust added and 25 cc. of glacial acetic acid added slowly with mechanical stirring; after standing at room temperature for twenty-four hours, the mixture was filtered to remove the excess of zinc and the filtrate poured into 500 cc. of cold water; the unreduced chloro-ethoxyquinazoline which precipitated was collected and recrystallized for recovery. The dilute alcoholic solution was made slightly basic by the addition of sufficient sodium hydroxide solution, which precipitated zinc hydroxide; the filtered solution (about 600 cc.) was then extracted with ether, the extract dried overnight with calcium chloride and the ether removed by distillation from a water-bath. The yellow oil which remained was distilled with steam the distillate extracted with ether, the ether solution dried with calcium chloride and the ether removed by distillation on a water-bath, removing the last traces of ether under a vacuum. As soon as the residual oil with a pleasant odor was poured on a watch glass it began to crystallize until the mass was almost completely solid; the material thus obtained was pressed between filter paper to remove traces of adhering oil and had a melting point of 46–48" (corr.); mixed with a known sample of 4-ethoxyquinazoline (m. p. 47–49°) prepared by the method of Bogert and May,[5] the mixture showed a melting point of 47–48°. Without further purification, this material obtained by the reduction with zinc and acetic acid was used for analysis.

Anal. Calcd. for $C_{10}H_{10}ON_2$: C, 68.93; H, 5.79. Found: C, 69.07; H, 5.81.

Reduction of 2-Chloro-4-methoxyquinazoline and **2-Chloro-4-phenoxyquinazoline.**—These reductions were made in alcohol with zinc and acetic acid as described above under the reduction of the analogous chloro-ethoxy derivative and in each case gave yellow-brown oils which did not crystallize on standing in a cold place; the product from the chloromethoxy derivative had a pleasant odor, whereas that from the chlorophenoxy derivative had a very disagreeable odor. Material of sufficient purity for analysis was not obtained.

Preparation of Benzoylene Urea (VI) by Hydrolysis **of Chloromethoxyquinazoline.**—Three grams of chloromethoxyquinazoline was suspended in 150 cc. of distilled water, warmed on the steam-bath for five hours, filtered, the insoluble portion washed with water, then with alcohol and dried; it was a white product which did not melt below 300°; it was submitted to analysis without further purification. The filtrate above gave a distinct test for chlorides and had a slight odor of methyl anthranilate.

Anal. Calcd. for $C_8H_6O_2N_2$: C, 59.22; H, 3.73. Found: C, 59.49; H, 3.87. Hydrolysis of chloro-ethoxyquinazoline similarly gave the same product.

Summary

A study has been made of the interaction of 2,4-dichloroquinazoline with sodium alcoholates in the presence of phenol and resorcinol and it was

found possible to replace but one of the two halogen atoms with an OR group (where R is either an alkyl or an aryl radical). The structure of the resulting compounds has been determined and shows that the halogen attached to the carbon atom at position 4 is more reactive than the halogen atom on carbon atom 2. Recrystallization of dichloroquinazoline from toluene or toluene plus petroleum ether yields a very pure product; these solvents are superior to benzene (which had been previously used in the preparation) because of the greater temperature coefficient of solubility. The following new compounds have been prepared: 2-chloro-4-methoxyquinazoline, **2-chloro-4-ethoxyquinazoline,** 2-chloro-4-phenoxyquinazoline and 2-chloro-4-resorcinoxyquinazoline.

CLEVELAND, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

THE PREPARATION OF CERTAIN GAMMA-LACTONES

BY WILLIAM L. NELSON AND LEONARD H. CRETCHER

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Gamma-butyrolactone was prepared by a method which involves (1) the condensation of the sodium salt of ethyl malonate with β-chloro-ethylvinyl ether to form ethyl vinyloxyethylmalonate,[1] (2) saponification of the ester, (3) liberation of the free acid with simultaneous hydrolysis and liberation of acetaldehyde to form β-hydroxyethylmalonic acid, (4) pyrogenic decomposition to the lactone of y-hydroxybutyric acid. The alpha-substituted ethyl and propyl butyrolactones were prepared in the same manner from the corresponding alkyl malonic esters.

Fittig and Chanlarow[2] prepared the a-ethyl derivative by hydrolysis of ethyl β-hydroxyethylacetoacetate. The unsubstituted lactone has been prepared by a variety of methods.[3]

It is interesting to note that in Pittig's description of a-ethyl butyrolactone he stated that a clear, approximately saturated water solution of the lactone on warming in the hand became clouded and remained so when placed in hot water until a temperature between 80–90° was reached, whereupon the second phase disappeared to reappear upon slight lowering of the temperature. When cooled more strongly, the solution again became clear. We have repeated Fittig's experiment with the same result. So far as the authors are aware, this is the first mention in the literature of a

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[1] Cretcher, Koch and Pittenger, THIS JOURNAL, 47,1173 (1925).

[2] Fittig and Chanlarow, *Ann.*, 226,327 (1884).

[3] (a) Frühling, *Monatsh.*, 3, 700 (1882); (b) Michael, *Ber.*, 34, 4053 (1901); (c) Henry, *Bull. soc. chim.*, [2] 45,341 (1886); (d) Bentley, Haworth and Perkin, *J. Chem. Soc.*, 69, 168 (1896); (e) Willstätter, *Ber.*, 35, 619 (1902); (f) Fittig and Roder, *Ann.*, 227, 23 (1885); (g) Marvel and Birkhimer, THIS JOURNAL, 51,260 (1929).

system having both upper and lower consolute points. This fact **has** been overlooked by those who have investigated closed solubility curves.[4]

The present authors have found that the system α-propyl-γ-butyrolactone–water has no determinable lower consolute temperature because of the separation of water in the solid phase before the lower critical temperature is reached.

Experimental Part

Preparation of **γ-Butyrolactone.**—44.5 g. of ethyl vinyloxyethylmalonate was added to a solution of 43 g. of potassium hydroxide in 35 cc. of water. The mixture was slowly warmed, with continual agitation, in a water-bath. At about 30° the saponification took place, the temperature going spontaneously to the boiling point of alcohol. After the vigorous reaction was over, the solution was heated on a water-bath for thirty minutes. After cooling 140 cc. of 1:1 hydrochloric acid was added and the solution evaporated to dryness under reduced pressure. The solid mass was cooled and extracted several times with anhydrous ether. The ether was removed by distillation and the distilling flask placed in such a position that the side-tube was inclined slightly upward. A short air condenser was attached to the side-tube and the flask was provided with a thermometer immersed in the solution. Water was removed by cautious heating over a direct flame.

The temperature was raised to 180° to decompose the dibasic acid and the product was then distilled. The yield of lactone boiling at 201–205° was 72% of the theoretical.

Brucine Salt of **γ-Butyrolacetone.**—The brucine salt of the unsubstituted hydroxybutyric acid offered no difficulties in purification. The salts of the ethyl and propyl substituted acids were not obtained in pure condition and will not be described.

The brucine salt was prepared by heating a water solution of the lactone with an excess of the alkaloid. The excess brucine was extracted with chloroform, the solution filtered through "Nuchar" and evaporated to dryness under reduced pressure. The salt was twice dissolved in 95% alcohol, cooled and precipitated with ether. It was then dried to constant weight, *in vacuo*, over phosphorus pentoxide. The compound softened at 80° and melted at 147–148°. It is very hygroscopic.

Anal. Calcd. for $C_{27}H_{34}O_7N_2$: N, 5.62. Found: N, 588, 562.

Optical rotation. 0.2579 g. in 10.08 cc. of aqueous solution in a 1-dm. tube gave $\alpha = -0.69''$; $[\alpha]^{25}_{D}$ $-26.97°$.

Sodium **γ-Hydroxybutyrate.**—It was stated by Marvel and Birkhimer[3g] that on neutralization of the lactone of γ-hydroxybutyric acid with sodium hydroxide a 40% yield of the sodium salt was obtained. In order to determine, if possible, the cause of their low yield of salt, we neutralized the lactone, with results as follows: the calculated amount of *N* sodium hydroxide was added to a hot aqueous solution of 1.509 g. of the lactone. The ring was easily opened, as the pink color due to a drop of phenolphthalein disappeared after several minutes. The solution was evaporated under reduced pressure to dryness and the residue dissolved in hot alcohol. On cooling part of the salt crystallized. The precipitation was completed by addition of ether. The product, dried over phosphorus pentoxide, weighed 1.960 g., corresponding to a yield of 89% of the theoretical.

Anal. Subs., 0.1644: Na_2SO_4, 0.0930. Calcd. for $C_4H_7O_3Na$: Na, 18.27. Found: Na, 18.32.

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[4] Cf. Cox, Nelson and Cretcher, THIS JOURNAL, 49,1080 (1927), for references to the literature of this subject.

When an excess of alkali was used for neutralization of the lactone a substance was formed which was not the sodium salt of the hydroxy acid. This substance was insoluble in alcohol or water.

α-Ethyl γ-Butyrolactone.—This compound was prepared from ethyl, ethylvinyloxyethyl malonate[6] in the same manner as y-butyrolactone except that the saponification was conducted in alcoholic solution. From 12 g. of the malonic ester 2.8 g. of product was obtained boiling at 214–218°. The yield was 59% of the theoretical.

α-Propyl-γ-butyrolactone was prepared as above from ethyl propylvinyloxyethyl malonate.[5] The product boiled at 230–235°; d_4^{25} 1.008. The yield was 63% of the theoretical.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.57; H, 9.45. Found: C, 65.23; H, 9.34.

Neutralization equivalent. Calcd.: 128.1. Found: 127.8.

Summary

A method is described for the preparation of y-butyrolactone and its a-alkyl derivatives.

PITTSBURGH, PENNSYLVANIA

(CONTRIBUTION NO. 68 FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

SYNTHESES IN THE PHENANTHRENE SERIES.
I. ACETYLPHENANTHRENES[1]

BY ERICH MOSETTIG AND JACOB VAN DE KAMP

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The preparation of 9-acetylphenanthrene was described by Willgerodt and Albert[2] in 1911. These authors obtained the substance by the Friedel–Crafts reaction, and describe it as fluorescent leaflets of melting point 123°. Analysis and the formation of an oxime and a phenylhydrazone showed the compound to be a phenanthryl methyl ketone. Oxidation with chromic acid led exclusively to 9,10-phenanthrenequinone, showing that the acetyl group occupied the 9-position on the phenanthrene nucleus. The authors do not mention the yields obtained, but from their description it is to be gathered that the ketone is very difficult to obtain in a pure state because of accompanying oils and tarry material.

In attempting to prepare 9-acetylphenanthrene according to Willgerodt's directions, we have obtained results differing considerably from those mentioned above. Acetylation of phenanthrene with acetyl chloride and aluminum chloride in carbon disulfide solution, under Willgerodt's conditions, gave a small amount of crystalline material, together with resinous products and a considerable quantity of a thin oil. From the oil a small quantity of a ketone could be isolated as the semicarbazone; the oil dis-

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[5] Cretcher, Koch and Pittenger, THIS JOURNAL, 47, 3033 (1925).

[1] These researches have been supported by the Committee on Drug Addiction of the National Research Council.

[2] Willgerodt and Albert, *J. prakt. Chem.*, [2] 84,383 (1911).

tilled almost undecomposed in vacuum but boiled over such a wide range that further investigation has been delayed.

The crystalline portion, which was obtained in a yield averaging 5 to 10% (in one experiment which could not be duplicated, 50–60%), melted from 60 to 80° and contained some phenanthrene. Since this could not be removed by crystallization, the mixture was treated with semicarbazide. The semicarbazone proved, however, to be heterogeneous, and from it by laborious fractional crystallization two different semicarbazones could be obtained. When these were decomposed with hydrochloric or oxalic acid, two ketones of m. p. 72 and 143° were isolated. It therefore seemed desirable to improve the method of preparation of the ketones.

Lowering the temperature to 0 or to –15° gave no better results; substitution of aluminum bromide and acetyl bromide decreases the yield; stannic chloride as catalyst, or acetic anhydride in place of acetyl chloride, according to Adams,[3] were likewise without favorable result.

When, however, nitrobenzene was used as a solvent, the mixture of ketones was obtained in about 80% yield. The separation of these was accomplished through the difference in solubilities in methyl and ethyl alcohol. The sparingly soluble ketone (yield 15%) melts at 143°, the more soluble isomer (yield 63.5%) at 72°.

To determine the position occupied by the acetyl group, the isomers were oxidized with 2% sodium hypochlorite solution according to Graebe[4] ($RCOCH_3 + 3\ NaOCl \longrightarrow RCOONa + 2\ NaOH + CHCl_3$), to the corresponding carboxylic acids.

The 72° ketone gave an acid of m. p. 270°, whose methyl and ethyl esters melted at 94.5–95' and 56–57', respectively. The acid gives a very characteristic potassium salt.

The 143° ketone yielded an acid melting at 258.5 to 260°, whose methyl and ethyl esters melted at 96–96.5' and 73–73.5°, respectively. The sodium salt is very sparingly soluble in water, the potassium salt nearly insoluble.

The properties of the acids, their esters and salts pointed to their identity with the phenanthrene-2- and 3-carboxylic acids of Werner[5] and Fieser.[6]

Phenanthrene-9-carboxylic acid, prepared according to Pschorr,[7] was found by direct comparison of properties and mixed melting points to be different from the acids prepared from the two ketones. Therefore, in neither of these ketones does the acetyl group occupy the 9-position.

[3] Adams and Noller, THIS JOURNAL, 46, 1889 (1024).

[4] Graebe, *Ber.*, **35**, 2753 (1902).

[5] Werner, *Ann.*, 321, 248 (1902), gives the m. p. 254" for phenanthrene-2-carboxylic acid, and emphasizes the slight solubility of the potassium salt. For the 3-carboxylic acid, the m. p. 269° is given.

[6] Fieser, THIS JOURNAL, **51**, 3101 (1929), gives the m. p of phenanthrene-7 carboxylic acid methyl ester as 974

[7] Pschorr, *Ber.*, 29, 497 (1896).

To prove that the acids derived from our two acetylphenanthrenes were actually the phenanthrene-2- and 3-carboxylic acids, these were synthesized by the method of Werner.[8]

Phenanthrene was sulfonated by Fieser's[9] modification of Werner's procedure. Under certain conditions, practically the only monosulfonic acids obtained are the 2- and 3-forms. The position of the sulfonyl groups in these acids, and consequently of the carboxyl groups in the carboxylic acids derived from them seems to be sufficiently proved by Werner's researches. That we were actually working with the pure sulfonic acids was proved by the preparation of the *p*-toluides (Fieser) and the methyl esters (Werner).

The phenanthrene-carboxylic acid prepared from the 2-sulfonic acid agreed in all characteristic properties and derivatives with that obtained by oxidation of the ketone melting at 143°; the carboxylic acid from the 3-sulfonic acid was similarly shown to be identical with the one obtained from our 72° ketone. On the basis of Werner's proof of the structure of these two sulfonic acids, therefore, we assign to the sparingly soluble ketone of melting point 143° the structure of 2-acetylphenanthrene; to the more soluble ketone of melting point 72°, the structure of 3-acetylphenanthrene.

Oxidation of the acetylphenanthrenes with chromic acid converts them smoothly into the 2-, and 3-acetylphenanthrene-9,10-quinones, respectively.

We have not yet been able to isolate any other acetylphenanthrene isomer from the reaction Very small amounts (0.1%) of a third substance, crystallizing in needles of melting point 279–280° were found, whose nature has not yet been determined.

Attempts to synthesize, from 9-substituted phenanthrene derivatives, the 9-acetylphenanthrene which was expected from Willgerodt's procedure have so far been fruitless. These experiments as well as those designed to introduce two acetyl groups and one or more benzoyl groups into the phenanthrene nucleus are being continued.

The marked favoring of the 2- and 3-positions observed in the above Friedel–Crafts acetylation over the 9-position, preference for which would be expected[10] from the presence of the 9,10-double bond, which recalls in many respects an olefinic double bond, is remarkable, and is not easy to bring into accord with the results of bromination,[11] nitration[12] and sulfonation.[13]

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[8] Ref. 5, pp. 326, 330.

[9] Fieser, THIS JOURNAL, 51,2460 (1929).

[10] Cf. Wieland and Bettag, "Zur Kenntnis der Friedel–Crafts'schen Reaktion," *Ber.*, 55,2246 (1922).

[11] Hayduck, Ann., 167, 180 (1873); *et al.*

[12] Schmidt, *Ber.*, 33,3251 (1900); Wieland and Rahn, *ibid.*, 54, 1770 (1921).

[13] Cf. Fieser, "The Sulfonation of Phenanthrene. II. Disulfonation," THIS JOURNAL, 51,2471 (1929)

It is possible that an investigation of the oil which appears in such large quantities in the customary procedure in carbon disulfide solution will give further information. The extent to which the nitrobenzene used as solvent influences the reaction in a qualitative or quantitative way is difficult to estimate.

Experimental Part

The phenanthrene used in the experiments described below was a purified product of m. p. 98–99°; the nitrobenzene was dried over calcium chloride.

2- and 3-Acetylphenanthrenes, $C_{14}H_9COCH_3$.—One hundred and thirty-two grams of finely powdered aluminum chloride was added in small portions to 600 g. of nitrobenzene, and the resulting clear solution then mixed with a solution of 80 g. of phenanthrene in 240 g. of nitrobenzene. The solution was cooled in ice water and 48 g. of freshly-distilled acetyl chloride was added all at once. After half an hour's standing in ice water, the dark clear solution stood at room temperature (25°) for six to seven hours. It was poured into a large amount of ice and treated with 80 cc. of concentrated hydrochloric acid. In all, 400 g. of phenanthrene, in five lots, was so treated, and the united products distilled with steam to remove nitrobenzene as completely as possible. The distillation residue was a dark brown viscous mass which on digestion with ether largely went into solution. The ether-insoluble portion, a dark crystalline mass, was purified in two ways.

(1) It was spread on a clay plate to remove oils and then refluxed with animal charcoal in methyl alcohol. From the filtrate the 2-acetylphenanthrene separated in nearly pure, faintly colored, thick needles, of m. p. 138–142°. The methyl alcohol-insoluble carbonaceous mass weighed 5 g. After two recrystallizations from methyl or ethyl alcohol or benzene, the ketone was obtained pure white, m. p. 143° (corr.).

(2) To avoid the purification with methyl alcohol, in which the 2-acetylphenanthrene is very sparingly soluble (benzene cannot be used, because it dissolves the impurities as well), the ether residue above was twice distilled at a pressure of 2–3 mm. in a sabre flask. The colorless distillate crystallized immediately and was purified from benzene. The two methods gave about the same yields.

3-Acetylphenanthrene, $C_{14}H_9COCH_3$.—The ethereal solution from extraction of the steam distillation residue above was dried over sodium sulfate and the ether distilled off. The residue solidified soon to dumps of crystals. From methyl alcohol this separated only as an oil; it was therefore extracted in a Soxhlet apparatus with petroleum ether (b. p. 40–60°), leaving a very small portion undissolved. After removal of the petroleum ether, the product was distilled at 2–3 mm., giving an oil which soon crystallized. This could be recrystallized from methyl alcohol, in which it is very soluble, yielding 3-acetylphenanthrene as clumps of needles, m. p. 72°.

In this crystallization a small amount (0.5 g.) of a nearly insoluble substance was obtained as long thin white needles of m. p. 279–280° (uncorr.), which has not yet been identified. Traces of the 2-acetyl compound were also found at this point.

From 400 g. of phenanthrene, 315 g. of pure 3-acetylphenanthrene (63.5%), 75 g. of pure 2-acetylphenanthrene (15%), and 0.5 g. of the 280° product were obtained.

2-Acetylphenanthrene is soluble with difficulty in methyl or ethyl alcohol, petroleum ether or ligroin, more soluble in benzene or glacial acetic acid.

Anal. Subs., 0.0777: CO_2, 0.2471; H_2O, 0.0397. Calcd. for $C_{16}H_{12}O$: C, 87.23; H, 5.50. Found: C, 86.73; H, 5.72.

2-Acetylphenanthrene **Semicarbazone.**—One-half gram of the ketone was dissolved in hot alcohol and treated with 10% more than the calculated amount of semicarbazide hydrochloride and sodium acetate in concentrated aqueous solution. The mixture was warmed for ten minutes and after a short time the semicarbazone separated crystalline. It crystallizes from alcohol, in which it is only slightly soluble, in leaflets. After drying in vacuum at 100°, it melted at about 260" with gas evolution, then solidified and melted again at 297–299° (uncorr.) with decomposition. The same melting phenomenon was shown in a vacuum melting point tube.

Anal. Subs., 4.994 mg.: 0.678 cc. of N (27°, 747 mm.). Calcd. for $C_{17}H_{15}ON_3$: N, 15.16. Found: N, 15.18.

2-Acetylphenanthrene **Phenylhydrazone.**—A hot glacial acetic acid solution of 0.5 g. of ketone was treated with a hot solution of 0.27 g. (10% excess) of phenylhydrazine in glacial acetic acid. The phenylhydrazone separated after a short time in faintly yellow, shining leaflets, which were washed with a little acetic acid; m. p. in evacuated tube, 187–188" (corr.), turning brown.

Anal. Subs., 5.009 mg.: 0.406 cc. of N (27°, 750 mm.). Calcd. for $C_{22}H_{18}N_2$: N, 9.03. Found: N, 9.10.

Oxidation with Chromic Acid

2-Acetylphenanthrene-9,10-quinone, $C_{14}H_7O_2COCH_3$.—One gram of ketone was warmed to solution in 20 cc. of glacial acetic acid and treated with 1.0 g. of chromic anhydride in 2 cc. of water and 5 cc. of glacial acetic acid, not permitting the temperature to rise above 80°. After ten minutes at 70–80°, the solution was cooled and the quinone separated as a fine crystalline precipitate. Recrystallized from glacial acetic acid, it formed fine orange-yellow needles, melting in vacuum at 223–224° (corr.) (sintering at 218").

Anal. Subs., 0.1015: CO_2, 0.2862; H_2O, 0.0389. Calcd. for $C_{16}H_{10}O_3$: C, 76.78; H, 4.03. Found: C, 76.90; H, 4.29.

Oxidation with Sodium Hypochlorite

Phenanthrene-2-carboxylic Acid, $C_{14}H_9COOH$.—A suspension of 3.0 g. of ketone in somewhat more than the calculated amount of 2% aqueous sodium hypochlorite solution was boiled gently for three hours. After an hour, the sparingly soluble sodium salt of phenanthrene-2-carboxylic acid began to separate. The odor of chloroform was perceptible during the reaction. At the end of the oxidation sufficient water was added to dissolve the salt and the unchanged ketone shaken out into ether. The acid was precipitated from the aqueous solution by hydrochloric acid; the yield of the crude dry product was 70% of the theoretical. It was recrystallized from glacial acetic acid, m. p. 258.5–260° (uncorr.). It was analyzed in the form of its esters.

Phenanthrene-2-carboxylic Acid Ethyl Ester.—One gram of the acid in 20 cc. of absolute alcohol with 1.5 g. of concentrated sulfuric acid was refluxed for three hours. After removal of most of the alcohol in vacuum, the residue was poured into a large amount of water, whereupon the ester separated crystalline. It was extracted into ether and freed from unchanged acid by shaking with dilute sodium hydroxide. The residue from the ether was recrystallized from petroleum ether as white needles of m. p. 73–73.5°. The yield was nearly quantitative.

Anal. Subs., 0.1289: CO_2, 0.3844; H_2O, 0.0695. Calcd. for $C_{17}H_{14}O_2$: C, 81.56; H, 5.64. Found: C, 81.33; H, 6.03.

Phenanthrene-2-carboxylic Acid Methyl Ester.—This was prepared by esterification with methyl alcohol, in the manner described above. It was recrystallized from methyl alcohol, and consisted of white needles, m. p. 96–96.5° (corr.), yield quantitative.

Anal. Subs., 0.1130: CO_2, 0.3363; H_2O, 0.0533, Calcd, for $C_{16}H_{12}O_2$: C, 81.32; H, 5.12. Found: C, 81,17; H, 5.28,

Phenanthrene-2-carboxylic Acid Amide, $C_{14}H_9CONH_2$.—The amide was prepared from the acid chloride by the action of ammonia. Five grams of the acid was boiled for one and one-half hours with five times the calculated amount of thionyl chloride. By evaporation of the excess thionyl chloride in vacuum, a slightly colored crystalline acid chloride resulted directly, which was used without further purification. One gram of the crude acid chloride was added to a solution of 0.5 g. of sodium hydroxide in 12 cc. of 20% ammonia. This was warmed for three and one-half hours on the steam-bath with frequent shaking and addition of two 5-cc. portions of 20% ammonia. The precipitate of the amide was filtered out and washed with water. Only traces of the carboxylic acid could be detected with hydrochloric acid in the filtrate. The amide crystallizes from methyl alcohol or benzene, in which it is sparingly soluble, in silky white needles of m. p. 242–243° (corr.).

Anal. Subs., 4.512 mg.: 0.259 cc. of N (25°, 755 mm.). Calcd. for $C_{15}H_{11}ON$: N, 6.33. Found: N, 6.53.

For comparison with the product obtained from oxidation of the 2-ketone, phenanthrene-2-carboxylic acid was prepared from barium phenanthrene-2-sulfonate.[5,6] This yielded on dry distillation with potassium ferrocyanide the phenanthryl-2-cyanide, agreeing in melting point with Werner's[6] cyanide (104.5–105° corr.). The acid obtained by hydrolysis of the cyanide was identical with that from the 2-ketone, as shown by mixed melting point and mixed melting point of the methyl esters. The extreme insolubility of the potassium salt is noteworthy.

3-Acetylphenanthrene, $C_{14}H_9COCH_3$.—Isolation as described above; m. p. 72°; white needles, quite soluble in methyl or ethyl alcohol, glacial acetic acid or benzene; soluble with difficulty in petroleum ether.

Anal. Subs., 0.0972: CO_2, 0.3100; H_2O, 0.0482. Calcd. for $C_{16}H_{12}O$: C, 87.23; H, 5.50. Found: C, 86.98; H, 5.55.

3-Acetylphenanthrene **Semicarbazone.**—White needles of m. p. 228–230° (corr.), sparingly soluble in alcohol.

And. Subs., 5.045 mg.: 0.689 cc. of N (29°, 749 mm.). Calcd. for $C_{17}H_{15}ON_3$: N, 15.16. Found: N, 15.21.

3-Acetylphenanthrene **Phenylhydrazone.**—Faintly yellow needles of m. p. 192.5–194° (corr.) in vacuum.

Anal. Subs., 4.845 mg.: 0.389 cc. of N (26°, 753 mm.). Calcd. for $C_{22}H_{18}N_2$: N, 9.03. Found: N, 9.08.

3-Acetylphenanthrene-oxime.—A solution of 1.0 g. of 3-ketone in 15 cc. of alcohol was treated with an aqueous solution of 0.7 g. of hydroxylamine hydrochloride *(2* moles), neutralized with sodium carbonate and refluxed for one hour. After filtering from the sodium chloride, the reaction mixture deposited needles; recrystallized twice from methyl alcohol, these melted at 143.5–144° (corr.).

Anal. Subs., 4.588 mg.: 0.241 cc. of N (24°, 754 mm.). Calcd. for $C_{16}H_{13}ON$: N, 5.96. Found: N, 5.99.

From the mother liquors from the preparation of the oxime a more soluble substance of m. p. 181–182° (uncorr.) could be obtained in very small quantities. It is possible that this represents a stereoisomeric oxime; the small quantity available was not obtained pure enough for analysis.

3-Acetylphenanthrene Picrate.—The picrate was obtained by mixing hot alcoholic solutions of the calculated amounts of the components. It consisted of bright yellow needles of m. p. 125–125.5° (corr.).

Anal. Subs., 5.079 mg.: 0.411 cc. of N (24°, 755 mm.). Calcd. for $C_{22}H_{15}O_8N_3$: N, 9.36. Found: N, 9.24.

Oxidation with Chromic Acid

3-Acetylphenanthrene-9,10-quinone.—The oxidation was carried out like that of the 2-ketone; because of its greater solubility, the quinone must in this case be precipitated out with water. It crystallizes in brick-red needle rosets from glacial acetic acid, m. p. 217–218.5° (corr.) in vacuum (sintering at 214°).

Anal. Subs., 0.1307: CO_2, 0.3681; H_2O, 0.0500. Calcd. for $C_{16}H_{10}O_3$: C, 76.78; H, 4.03. Found: C, 76.81; H, 4.28.

Oxidation with Sodium Hypochlorite

Phenanthrene 3-Carboxylic Acid.—The oxidation, carried out as in the case of the 2-acetyl compound, gave a 75% yield of the 3-carboxylic acid as white needles, very sparingly soluble in glacial acetic acid, and melting at 270° (uncorr.).

Phenanthrene 3-Carboxylic Acid Ethyl Ester.—White needles from petroleum ether, of m. p. 56–57' (corr.).

Anal. Subs., 0.1278: CO_2, 0.3829; H_2O, 0.0671. Calcd. for $C_{17}H_{14}O_2$: C, 81.56; H, 5.64. Found: C, 81.71; H, 5.88.

Phenanthrene 3-Carboxylic Acid Methyl Ester.—White needles from methyl alcohol, m. p. 94.5–95° (corr.). (Recently prepared by Fieser[6] from the silver salt and methyl iodide.)

Phenanthrene-3-carboxylic acid amide (prepared from the crude acid chloride) melts at 233–234° (corr.); Werner gives the melting point as 228° (uncorr.).

For comparison, phenanthrene-3-carboxylic acid was prepared according to Werner, from potassium phenanthrene-3-sulfonate, and was found to agree in properties. Potassium phenanthrene-3-carboxylate crystallizes in unusual form, hair-like needles, bowed into semicircular form. No depression was observed in a mixed melting point of the free acids, esters or amides.

Phenanthrene-9-carboxylic Acid Methyl Ester.—White needles from methyl alcohol, m. p. 116" (corr.).

Anal. Subs., 0.1155: CO_2, 0.3443; H_2O, 0.0562. Calcd. for $C_{16}H_{12}O_2$: C. 81.32; H, 5.12. Found: C, 81.30; H, 5.44.

Phenanthrene-9-carboxylic Acid hide.— The amide was prepared from the crude acid chloride with ammonia. It crystallizes from benzene in silky needles of m. p. 232–233° (corr.).

Anal. Subs., 5.145 mg.: 0.289 cc. of N (24°, 755 mm.). Calcd. for $C_{15}H_{11}ON$: N, 6.33. Found: N, 6.41.

Summary

The preparation of 2-acetylphenanthrene and 3-acetylphenanthrene in satisfactory yields has been described.

Through the smooth oxidation of the acetyl derivatives to the carboxylic acids, a good preparative way to phenanthrene-2-carboxylic acid and phenanthrene-3-carboxylic acid is opened.

UNIVERSITY, VIRGINIA

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

THE COMPOSITION OF AN ALDOBIONIC ACID FROM FLAXSEED MUCILAGE

BY ERNEST ANDERSON AND J. A. CROWDER

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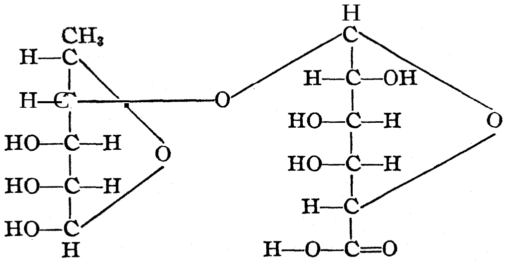
In 1903 Hilger[1] hydrolyzed flaxseed mucilage and found in the hydrolytic products the sugars d-glucose, d-galactose, *l*-xylose and *l*-arabinose, together with an acid by-product. In 1913 Neville[2] verified the work of Hilger on this mucilage. Abderhalden[3] states that this mucilage yields in addition to sugars, an acid complex which contains pentoses and hexoses.

The investigation reported in this paper deals with the aldobionic acid formed during the partial hydrolysis of flaxseed mucilage. This acid is composed of one molecule of d-galacturonic acid joined through its aldehyde group to a molecule of l-rhamnose. While the position of the oxide ring in the galacturonic acid and of the glucosidic union on the *l*-rhamnose have not been established, the following structure is suggested.



Experimental Part

Preparation of the Calcium Salt of the Aldobionic Acid.—Flaxseed mucilage was prepared according to the directions of Neville.[2,4] One kilogram of the air-dry mucilage was dissolved in 6 liters of 4% sulfuric acid and heated in a boiling water-bath for twenty hours. The solution was cooled, neutralized by excess calcium carbonate, heated in a boiling water-bath to complete the neutralization and filtered from the insoluble material. The filtrate was concentrated in *vacuo* to a volume of 1.5 liters, decolorized by norit and the salts precipitated in a large dish by addition of 3 volumes of 95% ethanol. After standing overnight with fresh 95% ethanol the salts were triturated with a pestle until granular, filtered, washed with alcohol and ether and dried on a porous plate. The yield was 340 g.

Purification and Analysis of the Calcium Salts.—The crude calcium salts were purified by the method of Levene.[5] For this purpose 340 g. of salts was dissolved in

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[1] Hilger, *Ber.*, 36, 3197 (1903).

[2] Neville, *J.* Ag. *Sci.*, 5, 113 (1913).

[3] "Biochemische Handlexikon," Julius Springer, Berlin, 1911, Band 2, p. 78.

[4] C. A. Morrow, "Biochemical Laboratory Methods," John Wiley and Sons, New York, 1927.

[5] Levene, J. *Biol.* Chem., 71,471 (1927); Goebel, *ibid.*, 72,813 (1927).

900 cc. of water, 1800 cc. of 95% ethanol added, the mixture heated in a boiling water-bath and then allowed to stand overnight. The clear supernatant liquid was decanted, concentrated in *vacuo* to a volume of 200 cc. and the salts precipitated by addition of 4 volumes of 95% ethanol. This was called salt "A." It weighed 24 g. Proceeding in the same general way, the solid residue was separated into fraction "B," weight 65 g., fraction "C," weight 60 g., and fraction "D," weight 75 g.

Samples of each of the above fractions were ground until they would pass an 80-mesh sieve and the analytical determinations described below then made.

Moisture.—Moisture was determined by drying 0.25-g. samples to constant weight in an Abderhalden vacuum drier using phosphorus pentoxide and a bath of boiling toluene.

Ash.—Calcium salts were burned at a low temperature and finally heated to constant weight over a blast lamp. Barium salts were burned at a low temperature but not heated over the blast. This gave barium carbonate. Barium was also determined as the sulfate in the regular way.

Uronic Acid.—The hexose uronic acid was determined by the method of Lefèvre.[6] This is an accurate determination. It is shown later that d-galacturonic acid is the uronic acid present. This can be determined approximately by oxidation to mucic acid by means of nitric acid but the method is not quantitative.[7]

Methyl Pentose.—It is shown later that *l*-rhamnose is present in the aldobionic acid; hence the percentage of this sugar is calculated from the pentosan determination. This determination was made according to the A. O. A. C.[8] Since the uronic acid yields furfural, the phloroglucide precipitate resulting from the decomposition of the uronic acid must be calculated, using the factor determined by Lefèvre.[9] When this calculated weight of phloroglucide is deducted from the total weight of phloroglucide, the remainder is the phloroglucide corresponding to the *l*-rhamnose present. From this weight the percentage of *l*-rhamnose hydrate is calculated using the table of Ellett.[10]

Since methyl furfural phloroglucide is soluble in alcohol, the percentage of *l*-rhamnose can also be determined by dissolving out the methyl furfural phloroglucide according to the method of Ellett and Tollens,[11] and Haywood.[12] It is well known that the methyl pentose determination is not accurate but merely an approximation.

The Aldehyde Group.—The percentage of aldehyde present, calculated as CHO, was determined by the method of Cajori.[13] This method was devised for the aldehyde group in mono and disaccharoses. Cajori states that the oxidation of glucose by iodine in sodium carbonate solution is complete in twenty-five minutes. Some sugars, however, require a longer time. The oxidation of the aldehyde group in the aldobionic acid under investigation required three hours for completion.

The purified calcium and barium salts of the aldobionic acid reduce Fehling's solution strongly. On the other hand, calcium and barium salts of the dibasic acid obtained by oxidation of the aldobionic acid with barium hypoiodite show no reduction of Fehling's solution.

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[6] A. W. van der Haar, "Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydesauren," Gebrüder Borntraeger, Berlin, 1920, pp. 71–76; Lefèvre and Tollens, *Ber.*, 40, 4513 (1907).

[7] Schorger, J. Ind. *Eng. Chem.*, 8, 498 (1916).

[8] "Methods of Analysis," A. O. A. C., 1925.

[9] Van der Haar, Ref. 6, p. 75.

[10] Van der Haar, Ref. 6, p. 82.

[11] Ellett and Tollens, Z. *deut. Zuckerind.*, 42, 19 (1905)

[12] Haywood, U. S. Bureau of Chemistry, Bull. 105, 1907, p. 112.

[13] Cajori, *J. Biol. Chem*, *54*, 617 (1922).

TABLE I

THE ANALYSIS OF CALCIUM SALT OF THE ALDOBIONIC ACID

Ftaction	Ash (CaO), %	CO_2, %	Galacturonic *acid* as mucic *acid*, %	*Methyl* pentose, %	*Reducing* sugar *as* CHO, %	$[\alpha]^{20}_{D}$
A	13.23	11.01	41.4	..	5.7	+92.0
B	12.07	11.27	39.45	35.3	5.57	+95.5
C	10.61	11.05	42.6	41.3	4.83	+94.4
D	10.16	11.27	48.7	37.2	4.70	+92.8

An inspection of the above table indicates little difference in the composition of the various fractions. Deviations in the analyses of the various fractions, particularly in the ash, were probably due to the presence of calcium sulfate as an impurity. The data approximate the theoretical for the calcium salt of an aldobionic acid consisting of one hexose uronic acid molecule and one molecule of a methyl pentose, but the results are not conclusive.

Identification of **the** Constituents of the Aldobionic Acid.—The naphthoresorcinol test and the yield of carbon dioxide by the method of Lefèvre proved the presence of a hexose uronic acid. This was identified as *d*-galacturonic acid by the method of Heidelberger and Goebel.[14] Twenty grams of fraction D salts was dissolved in 200 cc. of 6% hydrobromic acid containing 10 cc. of bromine. This mixture was heated under a reflux condenser in a boiling water-bath. After four hours a white crystalline precipitate began to form. After heating for ten hours the precipitate was filtered off and found to weigh 6.4 g. It was purified by dissolving in the calculated amount of dilute sodium hydroxide and reprecipitating with acid, and identified as mucic acid, melting point 210'.

The sugar present in the aldobionic acid would be oxidized in the above process to a monobasic acid and remain in the filtrate from the mucic acid. This filtrate was freed of excess bromine and hydrobromic acid and concentrated to a volume of 15 cc. To this solution was added 1 g. of phenylhydrazine hydrochloride. After twelve hours a light brown crystalline needle-like solid separated out. After recrystallization from hot ethanol the product melted at 193° and was identical with *l*-rhamnonic hydrazide.

To further establish the presence of I-rhamnose in the aldobionic acid, 20 g. of calcium salts D was dissolved in six times its weight of 4% sulfuric acid and hydrolyzed in the autoclave at a gage pressure of one atmosphere for six hours. The acids were removed from this solution by neutralizing with calcium carbonate, filtering, concentrating and precipitating the salts with alcohol. The alcohol solution of the sugars was concentrated in *vacuo* to a sirup. **A** portion of this sirup in water solution was not fermented by yeast, though when glucose was added it readily fermented. This proves the absence of glucose, mannose and fructose. The remainder of the sirup was oxidized by bromine to the monobasic acid and this acid converted to the phenylhydrazide, which did not crystallize until seeded with pure rhamnonic hgdrazide. This on re-

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[14] Heidelberger and Goebel, J. *Biol. Chem* , 74, 616 (1927).

crystallization from 95% ethanol gave crystalline needles melting at 193° and identical with *l*-rhamnonic phenylhydrazide.

Finally, crystalline *l*-rhamnose hydrate was isolated by hydrolysis of the acid, as follows. Fifty grams of mixed calcium and barium salts of the aldobionic acid was hydrolyzed in the autoclave and the sugar sirup isolated as already described. This sirup was decolorized by norit, all salts removed by solution in absolute alcohol and filtering, the solvent distilled off *in vacuo*, the gum dissolved in half its weight of water and an equal volume of glacial acetic acid added.[15] On seeding with *l*-rhamnose hydrate the mass became solid with crystals. The yield was 7 g. The melting point was 92–94° and the specific rotation was −7.8, constant after ten minutes.

Later experiments on the isolation of *l*-rhamnose hydrate from flaxseed mucilage indicate that the sirup must be fairly pure and contain small amounts of water. Salts and other impurities interfere with the crystallization.

Preparation and Analysis of the Barium Salt of the Aldobionic Acid.—Considerable difficulty was met in purifying the calcium salt of the aldobionic acid. Some calcium sulfate remained in all the fractions even after repeated precipitation of the salts. On the other hand, the barium salt in a fairly pure state can be more readily prepared. For this purpose 200 g. of the mucilage was mixed with six times its weight of 4% sulfuric acid and heated in a boiling water-bath for twenty hours. The acid was neutralized by the careful addition of barium hydroxide solution and an excess of barium carbonate. The barium sulfate was filtered off, the solution concentrated *in vacuo* and the barium salt isolated by precipitation with alcohol. The yield of salt was 40 g. This salt was purified by solution in water, a small amount of alcohol was added to precipitate a trace of gum and any suspended barium sulfate, the solution filtered and the pure barium salt precipitated by alcohol and analyzed.

Analysis of the Barium Salt of the Aldobionic Acid.—Barium determined as $BaCO_3$: found, 17.2%; calcd., 16.85%. Galacturonic acid from the CO_2 determination: found, 48.06%; calcd., 47.60%. Galacturonic acid from mucic acid determination: found, 41.92%; calcd., 47.60%. Aldehyde group: found, 7.09%; calcd., 7.11%. *l*-Rhamnose hydrate: found, 34.9%; calcd., 44.6%. Specific rotation, +79°.

The calculated percentages given above are for the barium salt of an aldobionic acid composed of one molecule of *d*-galacturonic acid and one molecule of *l*-rhamnose with the loss of one molecule of water. The experimental results check very closely with the theoretical values, except in the case of the mucic acid and methyl pentose determinations, both of which are known to be inaccurate methods.

Oxidation of the Aldobionic Acid to a Dibasic Acid.—Fifteen grams of the barium salt of the aldobionic acid was oxidized to the dibasic acid by means of barium hypoiodite.[5] The yield of the barium salt of the dibasic acid was 6.5 g. This salt did not reduce Fehling's solution but gave a positive naphthoresorcinol test and the following results on analysis: Ba as $BaSO_4$, found 24.8%; calcd., 26.00% galacturonic acid from CO_2 determination, found, 39.02; calcd., 39.46%—galacturonic acid from the mucic acid determination, found, 36.10%; calcd., 39.46%—specific rotation, +72°.

The Structure of the Aldobionic Acid.—The experimental work proves conclusively that the aldobionic acid consists of one molecule of *d*-galacturonic acid combined with one molecule of *l*-rhamnose. In this compound one aldehyde group is free and the other combined. If the aldehyde group of *l*-rhamnose is free and that of *d*-galacturonic acid is combined, then the dibasic acid formed by oxidation of the aldobionic acid with barium hypo-

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[15] Sands and Klaas, THIS JOURNAL, 51, 3441 (1929).

iodite would consist of d-galacturonic acid combined with *l*-rhamnonic acid. Such a compound would give a high percentage of carbon dioxide when heated with 12% hydrochloric acid, a low percentage of furfural and a positive naphthoresorcinol test. These are the results obtained. On the other hand, if in the aldobionic acid the aldehyde group of the d-galacturonic acid is free while the aldehyde group of the *l*-rhamnose is combined, then the dibasic acid formed by oxidation would consist of mucic acid combined with *l*-rhamnose. Such a compound would give no carbon dioxide, a high percentage of furfural and a negative naphthoresorcinol test, These results were not obtained. These facts prove conclusively that in the aldobionic acid the linkage is from the aldehyde group of the *d*-galacturonic acid to one of the secondary alcohol group of the 2-rhamnose.

Summary

Flaxseed mucilage yields on hydrolysis an aldobionic acid consisting of one molecule of d-galacturonic acid and one molecule of 1-rhamnose. The molecule is joined together by a glucosidic linkage involving the aldehyde group of the d-galacturonic acid and an alcohol group of the *l*-rhamnose. This mucilage is similar in composition and structure to some of the plant gums.

Further work on the structure of the mucilage is in progress.

TUCSON, ARIZONA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

PARA-PHENYLPHENACYL BROMIDE, A REAGENT FOR IDENTIFYING ORGANIC ACIDS[1]

BY NATHAN L. DRAKE AND JACK BRONITSKY

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Phenacyl bromide and the p-halogen substituted phenacyl bromides have been used with great success by Reid and his co-workers[2] for preparing esters which are excellently adapted for characterizing the organic acids therein combined. Such an ester may be prepared easily by the action of the bromide on the sodium salt of an acid in aqueous alcoholic solution; as a rule the ester crystallizes well and may be purified easily by a few crystallizations from aqueous alcohol. The reaction involved may be represented

$$p\text{-}XC_6H_4COCH_2Br + NaOCOR = p\text{-}XC_6H_4COCH_2OCOR + NaBr$$

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[1] **From a thesis submitted to the Graduate School of the University of Maryland by Jack Bronitsky in partial fulfilment of the requirements for the degree of Master of Science.**

[2] **Reid and co-workers, THIS JOURNAL, 41, 75 (1919); 42, 1043 (1920); 52, 818 (1930).**

The melting points of the esters from a given acid increase as X varies from hydrogen to chlorine to bromine to iodine. The iodophenacyl ester has the highest melting point, but in certain cases the melting point of even this derivative is so low as to make purification by crystallization difficult, particularly when small quantities of material are involved. Furthermore, with several acids Reid was unable to obtain a satisfactory solid derivative with any of the above-mentioned reagents.

The authors appreciated the facility with which the phenacyl esters may be prepared, but they desired a reagent which would yield, with certain acids containing highly branched chains, esters of melting points sufficiently high that purification by crystallization would be easy. A few tenths of a gram of acid would then suffice for its identification.

p-Phenylphenacyl bromide was consequently prepared, in the hope that the phenylphenacyl esters which could be derived from it would satisfy these requirements. Inasmuch as diphenyl is today a readily obtainable substance[3] and all the reactions involved in the preparation of the bromide give good yields, phenylphenacyl bromide is inexpensive and easy to prepare. Furthermore, examination of the properties of the esters obtained from a number of representative organic acids listed in the table clearly shows that in every case they compare favorably in melting point with the corresponding *p*-halogenated phenacyl esters. Of the ten acids which admit of comparison, the melting points of the p-phenylphenacyl esters are higher than those of the *p*-iodophenacyl esters in five instances, and do not differ by more than three degrees in two others. With only three acids out of eighteen, *viz.*, succinic, citric and caproic, were esters obtained which melted lower than the corresponding *p*-bromophenacyl esters, and the maximum difference was 6.6°—the *p*-phenylphenacyl ester of caproic acid melted at 65°, and the *p*-bromophenacyl ester melted at 71.6°. In addition, the solubility behavior of the phenylphenacyl esters is such that purification by crystallization is easily accomplished.

A more significant advantage of the new reagent lies in the fact that no carboxylic acid which we have so far investigated has failed to give a solid derivative. Referring again to the table, it is seen that of the twenty-four acids selected from those with which Reid worked, but eighteen yielded crystalline derivatives. *p*-Phenylphenacyl bromide, however, yielded a solid derivative in every case. It was not found possible to prepare the *p*-phenylphenacyl ester of benzene sulfonic acid in the usual way.

The procedure adopted for the preparation of p-phenylphenacyl esters was as follows. A weighed amount of acid (0.005 mole) was added to 5 cc.

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[3] Technical diphenyl is quoted in *Ind. Eng. Chem.*, for May, 1930, at 40 cents per lb. This substance is obtainable from the Federal Phosphorus Company of Birmingham, Alabama. The authors wish to express their thanks to this organization, which kindly supplied some of the diphenyl used in this research.

of water in a small Erlenmeyer flask, and then 0.0025 mole of sodium carbonate. The mixture was tested for acidity, and just enough more acid was added to make the solution acid to litmus; 10 cc. of alcohol was then put in, and if the salt of the acid was not thrown out of solution, 0.003 mole of the bromide was added and the mixture refluxed for an hour or more, depending on the acid involved.[4] If the acid salt was thrown out by the alcohol, a bit more water was added until the salt dissolved. The amounts of material recommended above yielded a quantity of ester which was sufficient, after purification, for elementary analyses. If only sufficient ester was desired for melting point comparisons, half of the amounts mentioned above yielded equally good results.

Some of the esters prepared were sparingly soluble in the reaction mixture and crystallized from the boiling solution. In the majority of cases, however, crystal formation did not take place until the reaction mixture was cooled, and in a few instances it was necessary to concentrate the solution to obtain a sufficiently large crop of crystals.

In most cases the ester formed rapidly, and many times a period of heating as short as twenty minutes was sufficient to bring about practically complete conversion of the acid salt into ester.

Certain dibasic acids whose sodium or potassium salts were sparingly soluble in aqueous alcohol of the requisite strength caused difficulty, and ester formation could not be brought about in the usual way. However, substitution of the methyl ammonium salts for the alkali salts made it possible to operate in such a fashion that at the outset all the reactants were in solution. When an ester was prepared in this way, it was found particularly important to have present a very slight excess of acid so that the reaction of the medium was not basic to litmus. If this precaution was not taken, colored by-products were formed which were very difficult to remove from the ester by subsequent recrystallizations. The ester prepared in the proper way was colorless.

In almost every case two recrystallizations of the crude ester proved ample to yield a substance whose melting point did not change on further crystallizations.

Experimental

Adam,[5] who first prepared phenylacetophenone, described his product as the 3-phenyl derivative. Vorlander,[6] however, showed that the compound which Adam prepared was probably 4-phenylacetophenone, and

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[4] Reid recommends refluxing monobasic acids for one hour, dibasic acids for two hours and tribasic acids for three hours; in many cases it is certain that when using *p*-phenylphenacyl bromide refluxing for a shorter period would be equally satisfactory.

[5] Adam, *Ann. Chim.*, [6] **15**, 255 (1888).

[6] Vorlander, *Ber.*, **40**, 4535 (1907).

later work has confirmed Vorländer's contention. Dilthey,[7] by oxidation of the benzal derivative of Adam's phenylacetophenone, obtained a diphenyl carbonic acid whose melting point and properties proved it to be identical with an acid prepared by Schlenk,[8] whose carbonyl was in the 4-position.

p-Phenylphenacyl bromide is not mentioned in the literature, although the corresponding chloride was described by Collet,[9] who prepared it by the Friedel and Crafts synthesis

$$C_6H_5C_6H_5 + ClCH_2COCl \xrightarrow{AlCl_3} C_6H_5C_6H_4COCH_2Cl + HCl$$

He describes the substance as a crystalline yellowish powder, soluble in alcohol, and possessing a melting point of 122–123°. Collet proved the location of the substituting group by oxidizing the chloro ketone to the corresponding acid. Collet's chloride was undoubtedly impure and should have been colorless.

p-Phenylphenacyl bromide was prepared by a method illustrated by the reactions

$$C_6H_5C_6H_5 + (CH_3CO)_2O \xrightarrow{AlCl_3} C_6H_5C_6H_4COCH_3 + CH_3COOH$$

$$C_6H_5C_6H_4COCH_3 + Br_2 \xrightarrow{CH_3COOH} C_6H_5C_6H_4COCH_2Br + HBr$$

It crystallizes in long colorless needles and melts sharply at 125.5'.

Preparation of *p*-Phenylacetophenone.—The procedure used in preparing this substance was a modification of that for the synthesis of acetophenone;[10] 0.8 mole (120 g.) of diphenyl, 1.76 mole (236 g.) of anhydrous aluminum chloride and 700 cc. of anhydrous carbon disulfide were placed in a two-liter three-necked flask provided with a mechanical stirrer, a dropping funnel and a reflux condenser holding a tube to carry off the evolved hydrogen chloride. The mixture was heated on the steam-bath until gentle refluxing started, and then 0.8 mole (85 g.) of acetic anhydride (b. p. 136–137°) was added. The addition of the anhydride required about an hour and the reaction mixture was refluxed gently for one hour after all of the anhydride had been added. When about three-quarters of the anhydride had been added, the addition product began to separate from the solution in the form of a curdy mass. Decomposition of the addition product was effected in the usual way by pouring the reaction mixture over ice and hydrochloric acid. The precipitate of *p*-phenylacetophenone was filtered on a Büchner funnel, washed several times with water, dried and distilled *in vacuo*. The carbon disulfide contains considerable of the ketone which can be recovered by evaporating the solvent. With very little forerunnings, the product boiled from 195 to 210° at 18 mm. pressure. The yield of distillate was 131 g. with a melting point of 118". Crystallization from alcohol yielded a product melting at 120–121° in an amount corresponding to 80% of that theoretically possible.

Preparation of *p*-Phenylphenacyl Bromide.—The procedure used was a modification of that described by Reid[11] for the preparation of the halogenated phenacyl bromides;

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[7] Dilthey, *J. prakt. Chem.*, [2] 101,194 (1920).

[8] Schlenk, Ann., 368,304 (1909).

[9] Collet, *Bull. soc. chim.*, 17, 510 (1897).

[10] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 19.

[11] Reid, THIS JOURNAL, 41, 77 (1919).

0.183 mole (36 g.) of p-phenylacetophenone was suspended in 200 cc. of glacial acetic acid, warmed gently on the steam-bath until a clear solution resulted, and then cooled as far as possible without the formation of crystals. To this solution was added slowly 0.183 mole (29.4 g.) of bromine. During the addition of the bromine, the temperature was not allowed to rise above 45°. When about three-quarters of the bromine had been added, the brominated product separated from the solution. After two hours, the flask was cooled in an ice- and salt-bath, the product filtered and washed with a bit of cold glacial acetic acid and two 50-cc. portions of cold water. The yield of crude material was 42 g., its melting point 124.5–125.5°. Recrystallization from hot 95% alcohol, with the addition of some activated charcoal to remove color, yielded a product melting at 125.5°. Approximately 6.7 g. of *p*-phenylphenacyl bromide dissolved in 100 cc. of boiling alcohol, and about 1.3 g. in 100 cc. of cold (25°) alcohol.

Table I

The Melting Points of a Few *p*-Phenylphenacyl Esters Compared with Those of Some Related Esters

Acid	Phenacyl ester	*p*-Chloro-phenacyl ester	*p*-Bromo-phenacyl ester	*p*-Iodo-phenacyl ester	*p*-Phenyl-phenacyl ester
Formic	oil	...	neg	neg.	74
Acetic	40	67.2	85	114	111
Propionic	...	...	59	94.9	102
Butyric	oil	...	63.2	81.4	97
n-Valeric	oil	...	63.6	78.6	63.5
Isovaleric	...	...	68.0	78.8	76
Caproic	...	...	71.6	81.5	65
Dimethylethylacetic	...	...	...	...	86.5
Heptylic	...	...	...	...	62
Caprylic	...	...	65.5	77.0	67
Lauric	48.9	70	76.0	...	84
Stearic	69	86	90	90.5	91
Oleic	oil	...	neg.	neg.	60.5
Monochloro-acetic	...	...	neg.	neg.	116
Maleic	119	...	neg.	...	168
Oxalic	oil	...	neg.	neg.	165.5 dec.
Succinic	148	197.5	211	...	208
Lactic	96	...	112.8	139.8	145
Mucic	...	...	neg.	...	149.5 dec.
Citric	104	...	148	...	146
Benzoic	118.5	118.6	119	126.5	167
o-Toluic	...	...	56.9	...	94.5
m-Toluic	...	...	108	...	136.5
p-Toluic	...	...	153	...	165
Cinnamic	140.5	...	145.6	...	182.5
Hippuric	...	...	151	...	163

In the table neg. means that the reaction did not occur, or yielded products of no significance. The leaders signify that data are not available. Compiled from data given by Reid, This Journal, **41,** 83 (1919); 42,1055 (1920); 52,818 (1930).

Summary

1. *p*-Phenylphenacyl bromide has been prepared.
2. This substance has shown itself to be well adapted for preparing

solid esters of organic acids. The properties of these esters render them useful in the identification of organic acids.

3. A number of representative esters have been prepared, and their melting points compared with those of the corresponding *p*-nitrobenzyl esters, phenacyl esters, and *p*-halogen phenacyl esters, where such comparison was possible.

COLLEGE PARK, MARYLAND

[A CONTRIBUTION FROM THE LABORATORIES OF THE UNIVERSITY OF MARYLAND AND THE U. S. INDUSTRIAL ALCOHOL COMPANY]

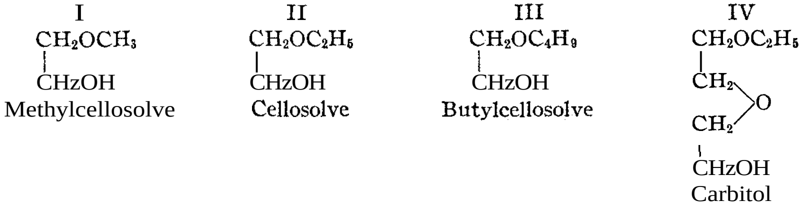
SOME REPRESENTATIVE CARBONATES AND CARBO-ETHOXY DERIVATIVES RELATED TO ETHYLENE GLYCOL[1]

BY NATHAN L. DRAKE AND RAY M. CARTER

RECEIVED JULY 8, 1930 PUBLISHED SEPTEMBER 5, 1930

Certain derivatives of ethylene glycol, in particular its ethers and esters, have become important in industry by reason of their solvent power for the cellulose esters. It seems strange, therefore, that there appears in the published literature no information regarding either the preparation or the properties of the carbonates and the carbo-ethoxy derivatives of the mono ethers of ethylene glycol. Allpress[2] describes some carbonates and carbo-ethoxy derivatives of ethylene glycol, but the corresponding mono ethers have apparently not been made.

It was decided, therefore, to study certain of these substances, in the hope that they might prove of value in the lacquer industry as plasticizers. The raw materials were



I $CH_2OCH_3-CH_2OH$ Methylcellosolve

II $CH_2OC_2H_5-CH_2OH$ Cellosolve

III $CH_2OC_4H_9-CH_2OH$ Butylcellosolve

IV $CH_2OC_2H_5-CH_2-O-CH_2-CH_2OH$ Carbitol

The carbonates were prepared by the reaction of phosgene and the glycol ether in a manner analogous to the preparation of alkyl carbonates. Phosgene was bubbled from a cylinder of the compressed gas into a weighed amount of the glycol ether in a tall narrow cylinder. The cylinder was immersed in a bucket of water in order that its temperature might be kept close to that of the laboratory, thus preventing the evolution of hydrogen chloride. At intervals the cylinder was removed and its increase in weight

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[1] From a thesis submitted to the Graduate School of the University of Maryland by Ray M. Carter in partial fulfilment of the requirements for the degree of Master of Science.

[2] Allpress, *J. Chem. Soc.*, 125,2259 (1924)

determined. When this increase indicated that the correct amount of phosgene had been introduced, the solution was heated, gently at first, then with increasing heat until boiling ensued.[3]

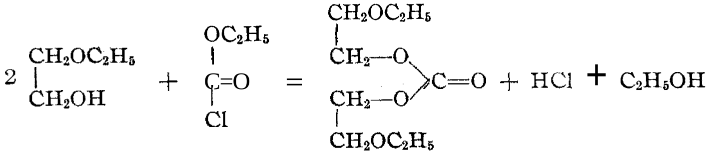
After the reaction was complete, the mixture was worked up in one of two ways: by washing with water, neutralizing with dilute sodium hydroxide, drying and fractionating, or by fractionating directly without preliminary neutralizing and drying.

In some cases this general method yielded unsatisfactory results. When methylcellosolve or carbitol were the starting materials, side reactions occurred between the hydrogen chloride and the ether, yielding halogen-containing products, among which was some alkyl chloride.

To obviate this difficulty, the glycol ether was first brought into reaction with metallic sodium and the resulting sodium glycolate treated with phosgene dissolved in benzene.

In preparing the carbo-ethoxy derivatives, ethyl chlorocarbonate was caused to react with the glycol ether. It was found early in the work, however, that a side reaction giving rise to considerable carbonate of the glycol ether occurred if the ether and chlorocarbonate were refluxed together.

Allpress[2] had noted earlier the formation of normal carbonate when ethylene glycol was heated with ethyl chlorocarbonate. In our case the reaction may be represented



$$2\begin{matrix}CH_2OC_2H_5\\ |\\ CH_2OH\end{matrix} + \begin{matrix}OC_2H_5\\ |\\ C{=}O\\ |\\ Cl\end{matrix} = \begin{matrix}CH_2OC_2H_5\\ |\\ CH_2{-}O\\ \\ CH_2{-}O\\ |\\ CH_2OC_2H_5\end{matrix}\!\!>C{=}O + HCl + C_2H_5OH$$

It was found, furthermore, that this side reaction could be minimized if the glycol ether was added dropwise to the ethyl chlorocarbonate boiling under reflux.

Here, also, certain of the glycol ethers yielded halogen-containing by-products, but in these cases the use of the sodium glycolate in benzene suspension obviated any difficulty.

All the compounds prepared had high boiling points, and preliminary experiments showed that it would be necessary to use a column that would maintain a high reflux ratio if good fractionation was to be accomplished. Two columns were used. One was 81 cm. from bottom outlet to side arm, the other 46 cm. Both were 2.5 cm. in internal diameter, the longer having a bottom outlet of 12 mm. internal diameter, and the shorter a bottom outlet of 19 mm. internal diameter. The longer of the two operated satisfactorily up to 225°, but above that point the lower outlet

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[3] Except in the case of diethylene glycol ether, IV, where the boiling point was very high.

was too small for the amount of liquid refluxing, and the column flooded. The shorter column was therefore made, provided with a wider outlet. It operated satisfactorily up to 300° at a distillation rate of 120 drops per minute and an estimated reflux ratio of 20:1. Both columns were heavily lagged with asbestos, corks were covered with tin foil, and short pieces of glass tubing were used to pack the columns. It was found unnecessary to use water in the depblegmator; while distilling the lower-boiling liquids, air was blown through the dephlegmator, but for the higher-boiling substances the air current was not necessary

The solvent action of the different preparations on three different cellulose esters was examined. The cellulose esters used were *(1) 20–30* second *R. S.* nitrocotton, *(2) 15* sec. *A. S.* nitrocotton, *(3)* cellulose acetate, *0.4* poise viscosity. These tests showed that both the carbonates and carbo-ethoxy derivatives of cellosolve, methylcellosolve and carbitol had high solvent power for both the A. S. and R. S. nitrocotton. The corresponding derivatives of the butyl ether were not such good solvents, the carbo-ethoxy derivative being somewhat better than the carbonate.

The only compounds which would dissolve cellulose acetate were the carbonate and carbo-ethoxy derivative of methylcellosolve. The other preparations merely swelled the cellulose acetate.

The high boiling points of some of these materials, particularly the derivatives of diethylene glycol, make them of interest as possible lacquer plasticizers.

Table I summarizes some of the properties of the compounds prepared. The percentage of ester was determined by saponification in a pressure bottle with $N/2$ alcoholic sodium hydroxide. The only change in the standard procedure was the addition of *100* cc. of water and *50* cc. of 10% barium hydroxide to the contents of the bottle before back titration with $N/2$ acid. Specific gravity was determined by means of a pycnometer. The boiling point was obtained by applying the proper stem and calibration correction to the temperature read during the fractionation. Refractive index was determined using an Abbé refractometer calibrated against distilled water.

TABLE I
PROPERTIES OF THE ESTERS

Carbonate	B. p., °C.	Mm.	% ester	Sp. gr.$^{25}_{4}$	n^{25}_{D}	Solvent action on R. S. nitrocotton	Solvent action on A. S. nitrocotton	Solvent action on Cellulose acetate
Ethyl (β-methoxyethyl)	182.1–183.1	760.4	99	1.0424	1.4036	Sol.	Sol.	Sol.
Di(β-methoxyethyl)	230.2–232.1	760.4	95	1.0936	1.4193	Sol.	Sol.	Sol.
Ethyl (β-ethoxyethyl)	194–194.9	762.7	97	1.0115	1.5064	Sol.	Sol.	Swells
Di(β-ethoxyethyl)	245.1–246.1	758.8	102	1.0635	1.4239	Sol.	Sol.	Swells
Ethyl (β-butoxyethyl)	223.9–224.4	759.0	95	0.9756	1.4143	Sl. sol. +	Sl. sol. +	Swells
Di(β-butoxyethyl)	297.2–298.2	761.7	95	0.9766	1.4279	Sl. sol.	Sl. sol.	Swells
Ethylcarbitol	242.7–244.2	764.4	101	1.0485	1.4203	Sol.	Sol.	Swells
Dicarbitol	231.9–234.9	55	95	1.0636	1.4353	Sol.	Sol.	Swells

Experimental

Di(β-methoxyethyl) Carbonate.—Seventy-nine and five-tenths grams of clean sodium was added to a solution of 300 g. of the monomethyl ether of ethylene glycol in 300 g. of benzene and a water-bath was used to bring the reaction to completion. To this mixture was added a benzene solution of phosgene, while the whole was kept cool in ice water. Phosgene was added until a distinct odor of it remained after shaking the reaction flask. Approximately 180 g. of phosgene was required. The salt which separated was dissolved by adding water and, after separation of the aqueous layer, the remaining oil was washed twice with 100-cc. portions of water. The product was dried over calcium chloride and distilled.

Ethyl (β-Methoxyethyl) Carbonate.—Five hundred grams of the glycol ether was added dropwise to 827 g. of ethyl chlorocarbonate boiling under reflux. After all of the ether had been added, boiling was continued for an hour. The crude was fractionated without a water wash or any further treatment.

Di(β-ethoxyethyl) Carbonate.—Gaseous phosgene was bubbled into a water-cooled cylinder containing 679 g. of glycol mono-ethyl ether until the weight increase was 339 g. The resulting solution was refluxed for four and one-half hours, washed with water, dried over calcium chloride and fractionated.

Ethyl(β-Ethoxyethyl) Carbonate.—Five hundred grams of glycol monoethyl ether was added slowly to 604 g. of boiling ethyl chlorocarbonate. Refluxing was continued for three hours after the addition of ether was completed. The resulting crude was fractionated without washing or neutralizing.

Di(β-butoxyethyl) Carbonate.—Two hundred and seventy-four grams of phosgene was bubbled into 717 g. of cooled ethylene glycol monobutyl ether. The solution was then boiled gently under reflux for three hours. After a water wash, it was dried over calcium chloride and fractionated.

Ethyl (8–Butoxyethyl) Carbonate.—Five hundred grams of ethylene glycol monobutyl ether and 460 g. of ethyl chlorocarbonate were mixed and boiled under reflux for four hours. After washing and drying, the product was fractionated. A considerable amount of di(β-butoxy ethyl) carbonate was obtained, showing this method of preparation to be inferior to that in which the glycol ether is added to boiling chlorocarbonate.

Dicarbitol Carbonate.—Three hundred and fifty-four grams of phosgene was dissolved in 903 g of cooled carbitol (IV) and the mixture allowed to stand for eighteen hours before heating. The solution was then heated for four hours at a temperature of about 200°. After a water wash, the washings were extracted with benzene and added to the main bulk of the product, whereupon all was dried over calcium chloride and fractionated in *vacuo.*

Ethylcarbitol Carbonate.—Fifty-eight and 8 tenths grams of sodium was brought into reaction with 300 g. of carbitol in 300 g. of benzene. Heating on a water-bath was necessary to complete the reaction. To this mixture was added a solution of 278 g. of ethyl chlorocarbonate in 300 g. of benzene. The salt which separated was dissolved in water and the water-insoluble layer washed with more water. After drying the product was fractionated.

Summary

1. The carbonates and carbo-ethoxy derivatives of the methyl, ethyl and butyl ethers of ethylene glycol, and of the ethyl ether of diethylene glycol, have been prepared and their boiling points, specific gravities and refractive indices determined.

2. All of the substances except those derived from the butyl ether of ethylene glycol have good solvent power for nitrocotton.

COLLEGE PARK, MARYLAND

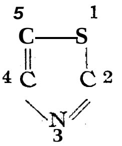
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE SYNTHESIS OF THIAZOLE AMINES POSSESSING PHARMACOLOGICAL INTEREST. IV

BY W. S. HINEGARDNER[1] AND TREAT B. JOHNSON

RECEIVED JULY 10, 1930 PUBLISHED SEPTEMBER 6, 1930

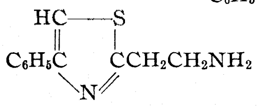
By bridging from carbon to carbon with a thiazole nucleus I in an aliphatic chain compound, it is theoretically possible to introduce structural features which make it practicable to study, from new points of view, the relationship between chemical constitution and physiological and pharmacological action. The thiazole nucleus I is chosen for such heterocyclic constructions because it contains both sulfur and nitrogen in cyclic linkage, and is a heterocycle which does not show high toxic effects when introduced into living organisms. Three distinct positions are available for carbon substitution in the ring (2,4,5), making it possible to obtain by synthesis interesting structural isomers for biological and clinical work. Furthermore, the thiazole cycle is a construction containing a stable molecular configuration with fined positions for the cyclic double bonds and with no possibility of structural alterations corresponding to lactam ⇄ lactim or keto ⇄ enol tautomeric changes. These same considerations apply also to heterocyclic combinations containing oxygen and selenium substituted in place of the thiazole sulfur, which will finally be included in our research program.



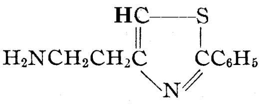
I

The organic constructions which are receiving our attention at present are the bridged thiazole derivatives of bases of the phenylethylamine type, II. It is a well-known fact that nucleus and side-chain substitutions in this base bring about pronounced physiological effects leading to products of therapeutic value. Our program calls for the study of compounds in which the aliphatic part is linked to the benzene nucleus by the thiazole ring, giving heterocyclic amines corresponding in structure to formulas III and IV. In this paper we shall report a practical procedure for preparing the new amine IV. In a later paper we shall describe a practical method for synthesizing the isomeric compound expressed by formula III.

$C_6H_5CH_2CH_2NH_2$ II



III



IV

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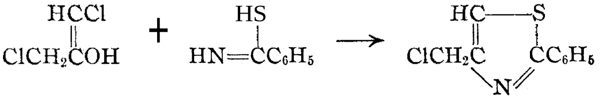
[1] Metz Research Fellow in Organic Chemistry, 1928–1929.

All the amines of this type, so far studied biologically, have been shown to be substances of decided pharmacological interest.

The starting points for this research were the halogenated ketone, *sym.*-dichloro-acetone V and thiobenzamide[2] VI. So far as the authors are aware, this halogen compound has been used hitherto for thiazole syntheses only by Suter and Johnson.[3] By interaction with thioamides it makes possible the preparation of interesting chlorine compounds, VII, containing the halogen in an aliphatic side chain or reactive position and useful for fundamental syntheses involving the application of the principle of alkylation.

Our method of operating has been to apply a malonic ester synthesis with the thiazole halide VII, obtaining first the ester VIII. In this operation a small amount of the disubstitution product IX is always formed. These esters are then saponified to form the corresponding malonic acids X and XI, and finally converted to the respective acetates XII and XIV according to fundamental organic technique. The hydrazides XVI and XXI and corresponding azides XVXI and XXII are then prepared and the latter transformed into the two ureas represented by formulas XVIII and XXIII. In order to obtain the corresponding amines these ureas are then fused with phthalic anhydride according to the technique of Manske and Ing[4] forming the phthalimide derivatives XIX and XXIV and the latter then converted into the required amines by treatment with hydrazine. In this manner we have prepared successfully the 2-phenylthiazole-4-ethylamine IV (XX in Tables I and II) and the interesting derivative of isopropylamine, namely. di-(2-phenylthiazole-4)-1,3-isopropylamine represented by formula XXV. The various compounds prepared in the course of our work and the fundamental experimental data identifying and characterizing the respective thiazoles synthesized are recorded in the two tables, I and II, respectively. A preliminary pharmacological study of these two amines together with other representatives of this series has already been started.



V VI VII

TABLE I

NOMENCLATURE AND CONSTITUTION (T = THE THIAZOLE NUCLEUS I)

VIII	Diethyl 2-phenylthiazole-4-methyl-malonate	$(C_2H_5OOC)_2CHCH_2TC_6H_5$
IX	Diethyl di-(2-phenylthiazole-4-methyl)-malonate	$(C_2H_5OOC)_2C(CH_2TC_6H_5)_2$
X	2-Phenylthiazole-4-methyl-malonic acid	$(HOOC)_2CHCH_2TC_6H_5$

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[2] Gabriel and Heymann, Ber., 23, 158 (1890).

[3] Suter and Johnson, Paper III, to appear in *Rec. trav. chim* (1930).

[4] Manske and Ing, J. *Chem. Soc.*, 128, 2348 (1926); Manske, THIS JOURNAL, 51, 1202 (1929).

TABLE I *(Concluded)*

XI	Di-(2-phenylthiazole-4-methyl)-malonic acid	$(HOOC)_2C(CH_2TC_6H_5)_2$
XII	2-Phenylthiazole-4-8-propionic acid	$HOOCCH_2CH_2TC_6H_5$
XIII	Ethyl 2-phenylthiazole-4-8-propionate	$C_2H_5OOCCH_2CH_2TC_6H_5$
XIV	Ethyl di-(2-phenylthiazole-4-methyl)-acetate	$(C_2H_5OOC)CH(CH_2TC_6H_5)_2$
XV	Di-(2-phenylthiazole-4-methyl)-acetic acid	$HOOCCH(CH_2TC_6H_5)_2$
XVI	2-Phenylthiazole-4-β-propionhydrazide	$H_2NNHCOCH_2CH_2TC_6H_5$
XVII	2-Phenylthiazole-4-β-propionazide	$N_3OCCH_2CH_2TC_6H_5$
XVIII	Di-(2-phenylthiazole-4-ethyl)-*sym.*-urea	$C_6H_5TCH_2CH_2NHCONHCH_2CH_2TC_6H_5$
XIX	2-Phenylthiazole-4-ethyl-phthalimide	$C_6H_4(CO)_2NCH_2CH_2TC_6H_5$
XX	2-Phenylthiazole-4-ethylamine	$H_2NCH_2CH_2TC_6H_5$
XXI	Di-(2-phenylthiazole-4-methyl)-acethydrazide	$H_2NNHCOCH(CH_2TC_6H_5)_2$
XXII	Di-(2-phenylthiazole-4-methyl)-acetazide	$N_3OCCH(CH_2TC_6H_5)_2$
XXIII	Tetra-(2-phenylthiazole-4)-1,3-isopropyl urea	$(C_6H_5TCH_2)_2CHNHCONHCH(CH_2TC_6H_5)_2$
XXIV	Di-(2-phenylthiazole-4)-1,3-isopropyl-phthalimide	$(C_6H_4(CO)_2NCH(CH_2TC_6H_5)_2$
XXV	Di-(2-phenylthiazole-4)-1,3-isopropylamine	$H_2NCH(CH_2TC_6H_5)_2$

TABLE II

EXPERIMENTAL DATA

Number	Solvent	Yield, %	M. p., °C.	B. p., °C.	Crystal form	Nitrogen, %		
						Calcd.	Found	
VII	Petroleum ether	81	31	155-156 (4 mm.)	Prisms	6.68	6.81	6.70
VIII[a]	Petroleum ether	54.1	30-31	218-222 (45 mm.)	Prisms	4.24	4.21	4.18
IX	Alcohol	34.7	116		Needles	5.53	5.49	5.51
X	Dil. alc.	98	141-142		Prisms	5.06	5.04	5.00
XI	Dil. alc. or acetone	85	156-157		Prisms	6.22	6.18	
XII	Alcohol	80	83-84		Needles	6.01	6.06	
XIII	Alcohol	86.6	42-43	170-171 (3-4 mm.)	Prisms	5.36	5.35	
XIV	Alcohol	80	61.5-62[b]	272° at (2-3 mm.)	Needles	6.45	6.55	
XV	Alcohol	80	127-128		Needles	6.89	6.81	
XVI	Alcohol	80	142-143		Prisms	17.01	17.3	17.4
XVII		90	72		Needles			
XVIII	Alcohol	85	176177		Plates	12.90	12.84	
XIX	Alcohol	87	113-114			8.38	8.24	8.34
XX[c]		76		146-147 (2-3 mm.)		13.72	13.71	13.67
XXI		75	Hydrochloride 235-238		Prisms			
XXII	Water	80	80					
XXIII	Alcohol	70	182-183		Prisms	10.76	10.57	10.62
XXIV	Alcohol	80	158-159		Plates	8.28	8.24	8.22
XXV	Alcohol	75	Hydrochloride 235-238		Needles	Cl, 21.89	Cl, 21.94	

[a] By using the sodium salt of diethylmalonate in 50% excess and by carrying on the synthesis at the temperature of boiling alcohol, the yield of the thiazole VIII was easily raised to 70% of the calcd. and with very little formation of the thiazole IX.

[b] Hydrochloride 91-92°.

[c] The monohydrochloride of this amine crystallizes as rhombic plates melting at 171–172° (calcd. Cl, 14.73. Found Cl, 14.77). The dihydrochloride crystallizes in needles and melts at 206–209°. (Calcd. Cl, 25.59. Found Cl, 25.41, 25.48.)

Experimental Part

2-Phenyl-4-chloromethyl Thiazole, VII.—This halide was prepared according to the method of Suter and Johnson.[3]

Diethyl-2-phenylthiazole-4-methyl Malonate, VIII.—For the preparation of this ester the usual technique applicable for a malonic ester synthesis was employed. By using 50% more than the calculated quantity of diethyl sodium malonate, the yield of monosubstituted ester VIII was raised to the maximum of 70%. The balance of the reaction product is the disubstituted ester IX, which is obtained in the form of a crystalline solid. This deposits from the crude ester reaction product on cooling at a low temperature. Both esters were carried through the same series of reactions and converted into the corresponding amines XX and XXV.

Saponification of these two esters with alcoholic potassium hydroxide led smoothly to the formation of the corresponding malonic acids. The latter on heating above their respective melting points are converted into the acetic acids XII and XV.

Preparation of the Hydrazides, XVI and XXI.—These are formed in excellent yields by digesting the esters XIII and XIV in alcohol with a slight excess of 40% hydrazine hydrate solution. The reaction requires for completion twenty to thirty hours of heating and the hydrazides are obtained in crystalline form without difficulty.

The hydrazides are converted into their corresponding azides by diazotization in glacial acetic acid solution. The latter were obtained in a crystalline condition and both compounds exploded with violence when heated above their respective melting points.

Summary

1. Using thiobenzamide and 2-phenylthiazole-4-chloromethyl thiazole as starting points in our synthetic research, twenty-four new thiazoles have been prepared.
2. The final products of the series of reactions recorded in this paper are the bridged thiazole amines—2-phenylthiazole-4-ethylamine and di-(2-phenylthiazole-4)-1,3-isopropylamine. Both of these bases are physiologically active substances.
3. Our work on thiazole amines is being continued.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ACTION OF BASES ON ALPHA,BETA-DIBROMO KETONES AND RELATED SUBSTANCES

BY E. P. KOHLER AND C. R. ADDINALL

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The reaction between α,β-dibromo ketones and bases has often been used for the preparation of other substances but has seldom been studied with care. It has the interesting peculiarity of yielding products so diverse that some of them can be hydrolyzed to 6-diketones while others serve as the basis of a very general method for preparing the corresponding α-derivatives.

The process leading to β-diketones was discovered by Sorge[1] and studied by Wieland,[2] who showed that the action of methyl alcoholic potassium hydroxide on one of these dibromides occurs in a number of steps which ultimately end in an acetal of a β-diketone.

$$p\text{-}NO_2C_6H_4CHBrCHBrCOC_6H_5 \longrightarrow p\text{-}NO_2C_6H_4C(OCH_3)_2CH_2COC_6H_5$$

The method of converting these dibromides into a-diketones was discovered by Dufraisse and Moureu.[3] After careful study these authors decided that the action of the base—in this case piperidine—must be represented by the following scheme

$$RCHBrCHBrCOR \longrightarrow RCH{=}CBrCOR \longrightarrow RCH_2C(NC_5H_{10})BrCOR \longrightarrow RCH{=}C(NC_5H_{10})COR$$

This scheme assumes a mode of addition of piperidine which is different from that which has been observed in every case in which a base or any other hydrogen compound has been added to an α,β-unsaturated ketone or ester. Dufraisse and Moureu attribute this "inverse" addition to the influence of the bromine in the a-position—a conclusion that has important theoretical consequences and which should, if possible, be confirmed. An examination of this mechanism was the principal object of our investigation.

The mode of attack was based on observations that were made while preparing a series of 6-diketones by the method of Sorge. In the course of these preparations it became evident that in many cases the yields are far from ideal because products are formed which cannot be hydrolyzed to β-diketones. Moreover, the solutions that are left, after removing the β-diketone completely as copper derivative, have a yellow color that is strongly suggestive of that of solutions of a-diketones. Since the reaction with piperidine has already been carefully studied by Dufraisse and Moureu, we decided to work with sodium alcoholates, and a casual observa-

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[1] Sorge, *Ber.*, 35, 1065 (1902).

[2] Wieland, *ibid.*, 37, 1148 (1904).

[3] Dufraisse and Mourcu, Bull. *soc. chim.*, [4] 41, 457 (1927).

tion led us to select the dibromide of benzal-*p*-bromo acetophenone for investigation.

When this dibromide was boiled with excess of methyl alcoholic sodium methylate, it formed a yellow solution from which after much manipulation we finally obtained two solids which separated from ether in large colorless crystals. These proved to be stereoisomeric acetals of a type very different from the one obtained by Wieland, namely,

$$C_6H_5CHOCH_3CHOHC(OCH_3)_2C_6H_4Br$$

These acetals constituted only about 40% of the products of the reaction, the remainder being composed of oils which on hydrolysis gave *p*-bromodibenzoylmethane. When sodium ethylate was substituted for the methylate all products were solid and it was possible to establish that the reaction leads almost exclusively to substances that are represented by the formulas

$$C_6H_5C(OC_2H_5){=}CHCOC_6H_4Br \text{ and } C_6H_5CHOC_2H_5CHOHC(OC_2H_5)_2C_6H_4Br$$

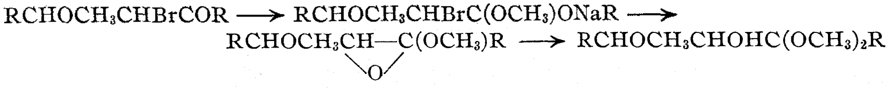
From these results it is clear that the reaction between α,β-dibromo ketones and alcoholates is not as simple as has been assumed. Following the course charted by Wieland, the dibromides first lose a molecule of hydrogen bromide to form an unsaturated a-bromo compound which in the alkaline solution combines with alcohol and forms a saturated bromo ether

$$RCHBrCHBrCOR \longrightarrow RCH{=}CBrCOR \longrightarrow RCHOCH_3CHBrCOR$$

Thus far all the dibromo ketones behave alike, and both the unsaturated and the saturated bromo compounds can be isolated when the solubility relations are favorable. Beyond this point the results depend upon the other groups present in the dibromides. In all the cases that we have examined some of the saturated bromo ether follows the course outlined by Wieland

$$RCHOCH_3CHBrCOR \longrightarrow RCOCH_3{=}CHCOR \longrightarrow RC(OCH_3)_2CH_2COR$$

Occasionally acetals of this type form the sole products of the reaction but this happens only when the dibromide has an unusually active hydrogen atom in the β-position as, for example, the *p*-nitro compound examined by Wieland and the ketonic esters studied by Rice.[4] In all other cases some of the saturated bromo ether reacts in a different manner



$$RCHOCH_3CHBrCOR \longrightarrow RCHOCH_3CHBrC(OCH_3)ONaR \longrightarrow RCHOCH_3\underbrace{CH{-}C}_{O}(OCH_3)R \longrightarrow RCHOCH_3CHOHC(OCH_3)_2R$$

The discovery that ethylene oxides may play a role in the reaction between bases and dibromo ketones supplies a basis for a new interpretation of the very interesting results of Dufraisse and Moureu. Our work on this phase of the problem has not been completed but in our opinion the course of the reaction between dibromo ketones and piperidine is quite different

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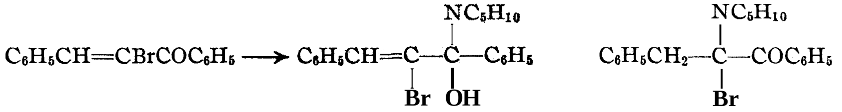
[4] Rice, THIS JOURNAL, **50**, 1481 *(1928)*.

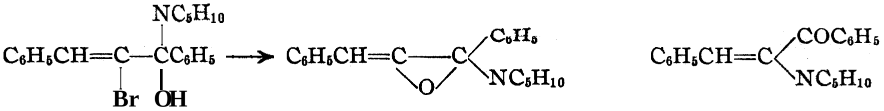
from that which was assumed by the French investigators. After the usual elimination of a molecule of hydrogen bromide the next step is 1,2-addition of piperidine to the carbonyl group. The result is the amine equivalent of a hemi-acetal; hence the great instability of the substance and the ease with which it loses hydrogen bromide—properties which appear to be quite inconsistent with the formula of Dufraisse and Moureu



$$C_6H_5CH{=}CBrCOC_6H_5 \longrightarrow C_6H_5CH{=}\underset{Br}{C}{-}\overset{NC_5H_{10}}{\underset{OH}{C}}{-}C_6H_5 \qquad C_6H_5CH_2{-}\overset{NC_5H_{10}}{\underset{Br}{C}}{-}COC_6H_5$$

D. and M.

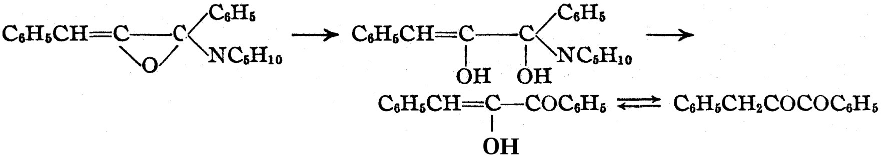
When this unsaturated bromohydrin is allowed to react with sodium methylate or a second molecule of piperidine, it undergoes the usual loss of hydrogen bromide and passes into an ethylene oxide



$$C_6H_5CH{=}\underset{Br}{C}{-}\overset{NC_5H_{10}}{\underset{OH}{C}}C_6H_5 \longrightarrow C_6H_5CH{=}C\underset{O}{\frown}C\begin{matrix}C_6H_5\\NC_5H_{10}\end{matrix} \qquad C_6H_5CH{=}C\begin{matrix}COC_6H_5\\NC_5H_{10}\end{matrix}$$

D. and M.

Like other ethylene oxides the product is capable of combining with bases, acetic acid and like substances. When it is hydrolyzed it inevitably passes into an a-diketone



$$C_6H_5CH{=}C\underset{O}{\frown}C\begin{matrix}C_6H_5\\NC_5H_{10}\end{matrix} \longrightarrow C_6H_5CH{=}\underset{OH}{C}{-}\underset{OH}{C}\begin{matrix}C_6H_5\\NC_5H_{10}\end{matrix} \longrightarrow$$
$$C_6H_5CH{=}\underset{OH}{C}{-}COC_6H_5 \rightleftharpoons C_6H_5CH_2COCOC_6H_5$$

In our opinion, then, Watson's brilliant red piperidine derivative is the first representative of an exceedingly interesting type of unsaturated ethylene oxide.[5] The twinning of the oxide ring with an ethylenic linkage results in a system that is almost as actively unsaturated as that of the ketenes. Like ketenes, therefore, it is highly colored, readily undergoes autoxidation and enters into a variety of reactions that involve the entire system.

Experimental Part

I. p-Bromo Series

Three substances were employed in the *p*-bromo series: the dibromide I, the α-bromo unsaturated ketone II, and the a-bromo-p-methoxy ketone III.

$$\underset{I}{C_6H_5CHBrCHBrCOC_6H_4Br} \quad \underset{II}{C_6H_5CH{=}CBrCOC_6H_4Br} \quad \underset{III}{C_6H_5CHOCH_3CHBrCOC_6H_4Br}$$

These substances were compared with respect to their behavior toward

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[5] Watson, *J. Chem. Soc.*, 85, 1322 (1904).

methyl alcoholic sodium methylate at the ordinary temperature and also at the boiling point; with two moles of the methylate and with thrice this quantity. The distribution of the material between the two types of reaction differed but little if any, but at the higher temperature there was considerable cleavage of the products which lead to the β-diketone, and the difficulty of isolating solid substances was correspondingly increased.

When the reactions are carried out at the ordinary temperature the result is a pale yellow solution. In order to get any solid from this solution it is necessary to remove the methyl alcohol completely, without allowing the solution to come in contact with acid, secure a solution in equal parts of dry ether and petroleum ether, and allow this to evaporate slowly through a tube that protects it against the acid fumes of the laboratory. It then, in time, usually begins to deposit one or two substances in colorless crystals which gradually grow to unusual dimensions and which can be readily separated mechanically. The first crystals are extremely difficult to secure, but once these are available crystallization can be induced immediately by inoculation.

The structure of these colorless products was established in the following manner. The analyses showed that the composition of both substances is represented by the formula $C_{18}H_{21}O_4Br$, that each has three methoxyl groups and one active hydrogen atom, and that neither has any other group capable of reacting with methyl magnesium iodide. These quantitative results indicate acetals with hydroxyl and a third methoxyl group strung on the chain of benzal-*p*-bromo-acetophenone. Gentle hydrolysis confirmed this conclusion because each substance gave a product which had but one methoxyl group, and along with it an active hydrogen and a group, presumably carbonyl, capable of reacting with one equivalent of methyl magnesium iodide.

In order to get substances more suitable for degradation, each of these hydrolysis products was treated with phenyl magnesium bromide. The result was two new substances and when these were cautiously oxidized with chromic acid, each yielded methyl benzoate and *p*-bromo-benzophenone. These transformations bear but one interpretation

$$\underset{\text{IV}}{C_6H_5CHOCH_3CHOHC(OCH_3)_2C_6H_4Br} \longrightarrow \underset{\text{V}}{C_6H_5CHOCH_3CHOHCOC_6H_4Br} \longrightarrow$$

$$\underset{\text{VI}}{C_6H_5CHOCH_3CHOHC(OH)(C_6H_5)C_6H_4Br} \longrightarrow C_6H_5CO_2CH_3 + CO_2 + C_6H_5COC_6H_4Br$$

The separation of the stereoisomeric trimethoxy compounds (IV) from the ethereal solution was, naturally, incomplete but it was possible to get a fairly accurate estimate of the quantities formed by hydrolyzing the entire product. The resulting β-diketone could be removed completely as its copper derivative, leaving only the isomeric hydrolysis products V which are stable and crystallize much more readily than the corresponding acetals.

Preparation of Materials.—The dibromide I has been described by Weygand,[6] who found a melting point of 184". Our material was repeatedly recrystallized from chloroform and melted at 187°. The a-bromo compound II has also been prepared by Weygand, who distilled it in a high vacuum and noted a boiling point of 136–143°. We found that it distils without decomposition at 230° under 3 mm.

Anal. Calcd. for $C_{15}H_{10}OBr_2$: C, 49.2; H, 2.7. Found: C, 49.2; H, 3.0.

α-Bromo-β-methoxy-benzyl-*p*-bromo-acetophenone, 111.—The bromo methoxy compound was made by the procedure of Middleton? A suspension of equivalent quantities of benzal-*p*-bromo-acetophenone and mercuric acetate in dry methyl alcohol was warmed until the clear colorless solution gave no test for mercuric acetate with alkali. The solution was then evaporated to a small volume. It deposited a solid which after recrystallization from acetone melted at 140°.

Anal. Calcd. for $C_{18}H_{17}O_4BrHg$: Br, 13.8. Found: Br, 13.9.

The mercury compound was suspended in dry methyl alcohol, the suspension was cooled to 0° and treated with an equivalent quantity of bromine. The mixture was set aside until all the color had disappeared, then evaporated in a current of air. It left a colorless oil. This was dissolved in ether, the solution freed from mercury salts by shaking with saturated potassium bromide solution, dried and evaporated. The product was an oil which would not crystallize and could not be distilled. A sample which had been kept in a vacuum desiccator for several weeks was analyzed.

Anal. Calcd. for $C_{16}H_{14}O_2Br_2$: C, 48.3; H, 3.5; OCH_3, 8.0. Found: C, 48.5: H, 3.5; OCH_3, 8.2.

The Isomeric Methyl Acetals, **IV.**—These acetals were first obtained by treating 200 g. of the dibromide in the manner described earlier in this section. One of them crystallized from ether in very large colorless prisms which melt at 90°; the other, which is formed in much smaller quantities, separated from petroleum ether in tables melting at 77". These substances were subsequently obtained more easily and in relatively larger quantities from the α-bromo compound II. The procedure was as follows.

A suspension of 50 g. of the bromo compound in 50 g. of dry methyl alcohol and a solution of 4.5 g. of sodium in 80 cc. of the same alcohol were cooled to 0° and mixed. The mixture was left to itself for three hours during which the temperature was allowed to rise to that of the room. The orange-colored solution was then evaporated under diminished pressure and the residue poured into ether and ice water. The ethereal layer was thoroughly washed with ice water, which reduced the color to a very pale yellow, then dried with calcium chloride, concentrated, mixed with an equal volume of low-boiling petroleum ether and inoculated with both acetals. It deposited in the course of a week 15.5 g. of the higher and 2 2 g. of the lower-melting acetal. The bromomethoxy compound III on similar treatment gave almost exactly the same results: 14.9 g. of the higher-melting and 2.0 g. of the lower-melting acetal from 50 g. of the bromo ketone.

Anal. Calcd. for $C_{18}H_{21}O_4Br$: C, 56.7; H, 5.5; OCH_3, 24.4. Found: (90°) C, 56.8; H, 5.6; OCH_3, 24.5. Found: (77°) C, 56.6; H, 5.5; OCH_3, 25.0.

The acetals are moderately soluble in petroleum ether, readily soluble in ether and other common organic solvents. Neither is stable in the air; the crystals of the higher-melting form gradually become opaque as they become covered with a film of the hydrolysis product and the lower-melting modification soon liquefies and then, as hydrolysis becomes nearly complete, resolidifies.

Hydrolysis.—When the acetals are hydrolyzed with dilute acetic acid, each gives

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[6] Weygand, *Ann.*, 459,118 (1927).

[7] Middleton, THIS JOURNAL, 45, 2763 (1923).

but one compound, while treatment with methyl alcoholic hydrochloric acid generally gives a mixture of both hydrolysis products. A solution of 5 g. of the higher-melting isomer in 25 g. of glacial acetic acid was diluted with an equal volume of water, and then digested on a steam-bath for thirty minutes. The clear colorless solution, on dilution, precipitated a colorless oil. This was collected in ether. The washed and dried ethereal solution on evaporation deposited a colorless solid which separated from ether–petroleum ether in stout needles or plates melting at 89°.

Anal. Calcd. for $C_{16}H_{15}O_3Br$: C, 57.3; H, 4.5; OCH_3, 9.2. Found: C, 57.2; H, 4.7; OCH_3, 9.4.

The lower-melting isomer, when treated in the same manner, gave a product which crystallized in tables or stout prisms and melted at 96°.

Anal. Calcd. for $C_{16}H_{15}O_3Br$: C, 57.3; H, 4.5; OCH_3, 9.2. Found: C, 57.1; H, 4.8; OCH_3, 8.7.

In the machine[8] these isomeric hydrolysis products behaved alike; each consumed two moles of reagent and liberated one mole of gas.

The Grignard Products, α-Phenyl-α-methoxy-β-hydroxy-γ-phenyl-γ-(4-bromophenyl)-γ-hydroxy-propane, VI.—An ethereal solution of 1.5 g. of the hydrolysis product (89°) was added to a solution of phenyl magnesium bromide prepared from 1 g. of magnesium. The mixture was boiled for fifteen minutes and then decomposed with iced acid. After the usual manipulations the operation yielded 1.5 g. of a solid product which crystallized from ether–petroleum ether in fine needles and melted at 119–120°.

Anal. Calcd. for $C_{22}H_{21}O_3Br$: C, 64.0; H, 5.1; OCH_3, 7.5. Found: C, 64.0; H, 5.3; OCH_3, 7.5.

The glycol is sparingly soluble in petroleum ether, readily soluble in ordinary ether and in methyl alcohol. It is very readily oxidized by chromic acid. A solution of 0.45 g. of the substance in 20 g. of glacial acetic acid was warmed to 70°. Into this solution was dropped an aqueous solution of chromic acid as long as the color disappeared immediately. The solution was then poured into cold water, which precipitated a crystalline solid. This was identified as pure p-bromobenzophenone by comparison with a sample on hand. The filtrate from the ketone was saturated with salt and extracted with ether. The ethereal solution, freed from acids by extraction with bicarbonate, was evaporated. It left an oil which was identified as methyl benzoate by the odor and by hydrolysis to benzoic acid.

The isomeric hydrolysis product (96°) was also treated with phenyl magnesium bromide but failed to give a crystalline product. The colorless oil that was left after evaporating the ethereal solution was therefore oxidized with chromic acid. Like its isomer it yielded p-bromobenzophenone, methyl benzoate and no other products. The hydrolysis products and the acetals from which they are formed must, therefore, be stereoisomers.

The Ethyl Acetal, $C_6H_5CHOC_2H_5CHOHC(OC_2H_5)_2C_6H_4Br$.—When the dibromide of benzal-p-bromo-acetophenone was shaken with excess of cold sodium ethylate it yielded, after the usual manipulation, a pale yellow solution that ultimately solidified almost completely. The solid was composed mainly of β-ethoxy-benzal-*p*-bromoacetophenone and an acetal. The unsaturated ethoxyl compound was readily isolated because it is far less soluble than the acetal but the isolation of pure acetal required patient fractional crystallization. It separates from petroleum ether in large colorless plates and melts at 99°.

Anal. Calcd.: C, 59.6; H, 6.4; OC_2H_5, 31.9. Found: C, 59.8; H, 6.6; OC_2H_5, 30.6.

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[8] Kohler and Richtmyer, THIS JOURNAL, 52, 3736 (1930).

Hydrolysis, $C_6H_5CHOCH_2CH_5OHCOC_6H_4Br$.—The acetal, like the corresponding methoxyl compounds, is unstable in the air of the laboratory; it first liquefies, then resolidifies. The solid is the pure hydroxy ketone. This is easily obtained in quantity by hydrolyzing the acetal with dilute acetic acid in the usual manner. It is readily soluble in all organic solvents, crystallizes in needles and melts at 72°.

Anal. Calcd. for $C_{17}H_{17}O_3Br$: C, 58.4; H, 4.9; OC_2H_5, 12.9. Found: C, 58.4; H, 5.2; OC_2H_5, 14.2.

β-Ethoxy-benzal-*p*-bromo-acetophenone, $C_6H_5C(OC_2H_5){=}CHCOC_6H_4Br$.—The ethoxyl compound crystallizes well from all solvents, separating in plates from methyl alcohol and in very large tables from ether and from petroleum ether. It melts at 112° and on hydrolysis yields *p*-bromodibenzoylmethane.

Anal. Calcd. for $C_{17}H_{15}O_2Br$: C, 61.6; H, 4.5. Found: C, 61.7; H, 4.6.

II. Other Dibromides

A. p-Nitro Compounds

The behavior of a few other dibromides was examined for the purpose of ascertaining how the distribution of the material is affected by the presence of substituents in the phenyl groups. Wieland[2] treated the dibromide of *p*-nitro-benzalacetophenone (VII) with methyl alcoholic potassium hydroxide and obtained only the dimethyl acetal of *p*-nitrodibenzoylmethane. We employed sodium methylate and extended the experiments to include the two stereoisomeric unsaturated a-bromo compounds VIII, and the bromo methoxyl compound IX. All of these substances yielded at least 95% of the acetal obtained by Wieland.

$$NO_2C_6H_4CHBrCHBrCOC_6H_5$$

VII

$$NO_2C_6H_4CH{=}CBrCOC_6H_5$$

VIII

$$NO_2C_6H_4CHOCH_3CHBrCOC_6H_5$$

IX

a-Bromo-finitrobenzalacetophenone, VIII.—Weygand[9] boiled the dibromide VII with methyl alcoholic potassium acetate for eight hours and distilled the product in a high vacuum. He obtained an a-bromo compound that melted at 106°. This was evidently a mixture of the two stereoisomers. We suspended the dibromide in a mixture of equal volumes of acetone and methyl alcohol, added excess of potassium acetate and allowed the reaction to proceed in the cold. All the dibromide disappeared within an hour. The solution was evaporated in a current of air. It left an oil that soon solidified. By systematic fractional crystallization from acetone–methyl alcohol mixtures the solid was separated into pale yellow needles melting at 130° and darker yellow plates that melted at 62°.

Anal. Calcd. for $C_{15}H_{10}O_3NBr$: C, 54.2; H, 3.0. Found: (136°) C, 54.6; H, 3.1. (62°) C, 54.2; H, 3.1.

The Bromo Methoxy Compound IX.—The preparation of this substance is exceedingly difficult because the reaction between the unsaturated ketone and mercuric acetate is both slow and incomplete even in boiling methyl alcohol. The mercury compound was not purified but treated directly with bromine. The product crystallized from acetone and methyl alcohol in colorless plates melting at 131°.

Anal. Calcd. for $C_{16}H_{14}O_4NBr$: C, 52.7; H, 3.8. Found: C, 52.8; H, 4.0.

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[9] Weygand, Ref. 6, p. 116.

All three of these compounds were treated with sodium methylate in the usual manner, but instead of attempting to isolate the acetals, the entire product was hydrolyzed with acetic acid. The residue left after removing the β-diketone as copper derivative in no case equaled 5% of the bromo compound that was used.

B. *m*-Nitro Compounds

In the m-nitro series we examined only the dibromide and the bromo methoxy compound. The former has been described by others; the latter was prepared as usual, by way of the mercury compound.

A suspension of 20 g. of the unsaturated ketone and an equivalent quantity of mercuric acetate in 500 cc. of dry methyl alcohol was boiled for twelve hours. The clear very pale yellow solution was concentrated step by step. It gradually deposited 20 g. of the mercury compound, which crystallized from acetone in hard nodules of colorless needles, sparingly soluble in ether and in methyl alcohol, readily soluble in acetone.

The mercury compound was suspended in methyl alcohol and treated with bromine. The reaction was very sluggish but the mercury compound gradually disappeared at the boiling point. The product, a colorless solid, was recrystallized from methyl alcohol.

Anal. Calcd. for $C_{16}H_{14}O_4NBr$: C, 52.7; H, 3.8. Found: C, 53.0; H, 4.0.

α-Bromo-β-methoxy-*n*-nitrobenzylacetophenone, $NO_2C_6H_4CHOCH_3CHBrCOC_6H_5$, is sparingly soluble in cold methyl alcohol, moderately soluble in hot methyl alcohol, readily soluble in acetone. It crystallizes from methyl alcohol in colorless needles melting at 132°. The yield was 80%.

α-Hydroxy-β-methoxy-*n*-benzylacetophenone, $NO_2C_6H_4CHOCH_3CHOHCOC_6H_5$.—The dibromide and the bromomethoxy compound were treated with sodium methylate in the usual manner, and in each case the mixture of products was immediately hydrolyzed with aqueous acetic acid. The ethereal solutions left after removing the *P*-diketone as copper derivative deposited the hydroxy ketone as a colorless solid. The substance was purified by recrystallization from ether–petroleum ether, from which it separated in colorless prisms melting at 110°. The yield from the dibromide was 30% and from the bromomethoxy compound 33%. As would be expected, the nitro group in the meta position has little influence.

Anal. Calcd. for $C_{16}H_{15}O_5N$: C, 63.8; H, 5.0. Found: C, 64.1; H, 5.2.

C. Anisyl Compounds

The behavior of the dibromide of benzalacetylanisole toward sodium methylate has been examined by Weygand[10] but we included it in our experiments because we expected it to be at least as favorable for the formation of the new type of acetal as the corresponding *p*-bromo compound. We have been unable to establish this because we did not succeed in getting either the acetal or its hydrolysis product in a crystalline form. In another respect, however, the behavior of the dibromide was gratifying; it provided the first case in which the dibromide could be transformed directly into the α-bromo-β-methoxy derivative.

α-Bromo-β-methoxy-benzylacetylanisole, $C_6H_5CHOCH_3CHBrCOC_6H_4OCH_3$.—A solution of 6 g. of sodium in 120 g. of anhydrous methyl alcohol was added to a suspension of 43.5 g. of the dibromide in 75 cc. of the same solvent. The mixture was shaken

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[10] Weygand, Ref. 6, p. 107.

vigorously until solution was complete, then cooled first in ice water and finally in a freezing mixture. It deposited 30 g of a mixture of solids which was readily separated by recrystallization from methyl alcohol. The principal product was sparingly soluble in methyl alcohol but was readily recrystallized from a mixture of acetone and methyl alcohol from which it separated in colorless plates melting at 126°.

Anal. Calcd. for $C_{17}H_{17}O_3Br$: C, 58.5; H, 4.9. Found: C, 58.4; H, 5.0.

The bromomethoxy compound was obtained even more readily by shaking a suspension of α-bromo-benzalacetylanisole in anhydrous methyl alcohol containing a small quantity of sodium methylate. In the hope of getting a stereoisomeric bromomethoxy compound we also added mercuric acetate to benzalacetylanisole and brominated the product, but these operations gave the same bromo compound. This substance was, doubtless, also obtained by Weygand by boiling a suspension of the dibromide with methyl alcoholic potassium hydroxide. Weygand naturally assumed that the product would be an α-bromo-benzalacetylanisole and attributed his analytical results to the difficulties met with in the analysis of methoxyl compounds.

The remainder of the solid product was a mixture which was separated by recrystallization from ether and petroleum ether into the α-bromo and β-methoxy derivatives of benzalacetylanisole. These substances have been accurately described by Weygand.

A solution of the bromomethoxy compound in methyl alcohol was shaken with an excess of sodium methylate for thirty-six hours. The product was isolated in the usual manner but failed to give any solid compounds. It was therefore hydrolyzed with aqueous acetic acid. It yielded the diketone (about 70%) and an oil from which it has not as yet been possible to obtain any solid compounds.

Summary

1. α,β-Dibromo ketones may react with alcoholates in two different ways which ultimately lead to very different types of acetals

$$RC(OR)_2CH_2COR' \longleftarrow RCHBrCHBrCOR' \longrightarrow RCH(OR)CHOHC(OR)_2R'$$

2. Most dibromo ketones yield both acetals, but when the hydrogen in the β-position is unusually active, the acetal of a β-diketone may be the only product.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE "MACHINE" FOR ANALYSIS WITH GRIGNARD REAGENTS

BY E. P. KOHLER AND N. K. RICHTMYER

RECEIVED AUGUST 12, 1930 PUBLISHED SEPTEMBER 5, 1930

Since the appearance of the original paper on an "apparatus for determining both the quantity of gas evolved and the amount of reagent consumed in reactions with methyl magnesium iodide,"[1] the apparatus has been redesigned and considerably improved. In view of a steadily increasing number of inquiries, dealing largely with the special stopcock, it seems desirable to publish the new design and to show how this beautiful but troublesome stopcock has been eliminated.

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[1] Kohler, Stone and Fuson, THIS JOURNAL, 49, 3181 (1927).

By introducing the reagent into the top of the buret we have been able to use an ordinary two-way stopcock which comes in contact with the reagent at but one point, hence can often be used for a month or more without being regreased. In redesigning the apparatus we also eliminated the ground-glass joint at the top of the reservoir A and improved the shoulder, *i*, in order to secure a better control of the temperature of the gas inclosed in the shoulder.

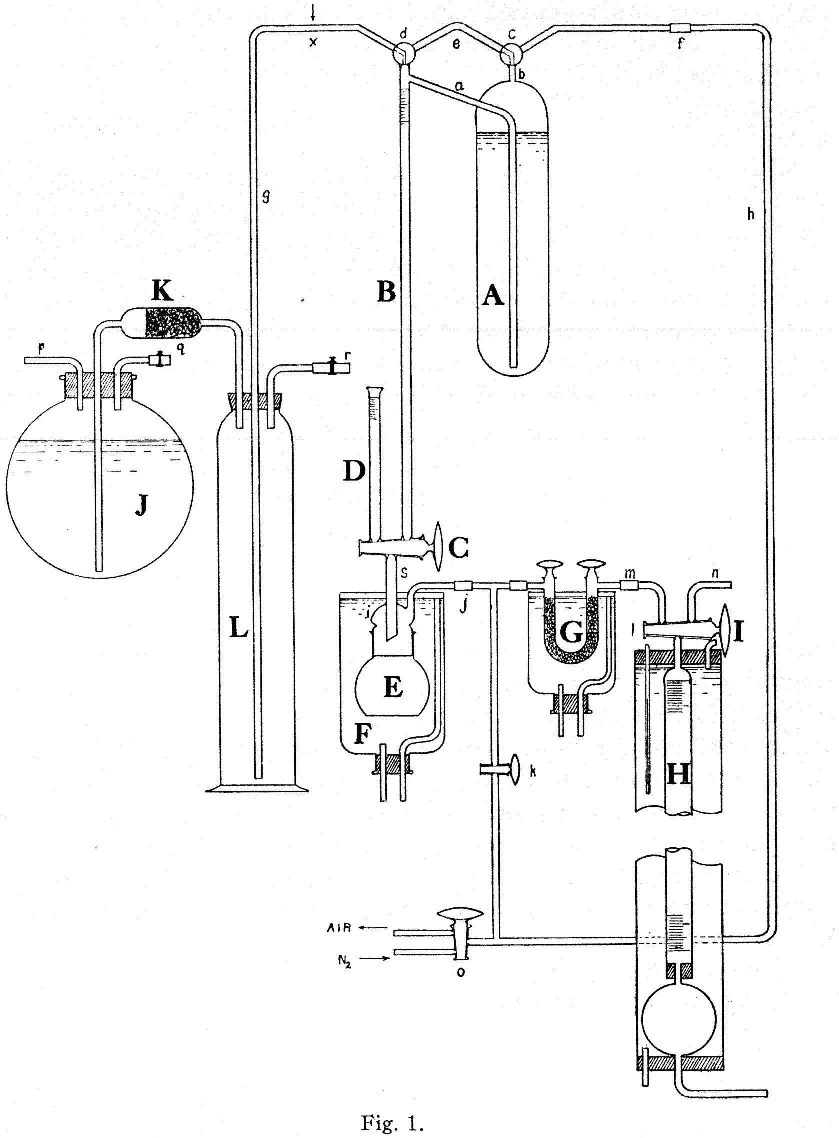

Fig. 1.

These alterations do not necessitate any serious changes in the operation of the machine. In order to clean the reservoir it is now necessary to dismount the entire machine but since a single charge serves for about a hundred analyses we do not regard this as a serious matter. After filling the reservoir we cut the tube g at x and clean the small section between x and d with a pipe cleaner. This leaves a light, compact apparatus which is relatively free from strain, and which we hold with a single clamp on the reservoir.

The reagent is now pressed from the reservoir to the reagent buret through a. After the desired amount has been introduced into the buret the stopcocks c and d are turned to open the reservoir to the air for an instant; this relieves the excess pressure in A. Then c and d are turned in such a manner that the nitrogen presses the reagent remaining in a, back into the reservoir, after which **A** is again momentarily opened to the air. All stopcocks can be removed, cleaned and regreased in a properly directed current of nitrogen without affecting the titer of the solution. It is well also to sweep the system o–k–j–i with nitrogen while spraying the shoulder i with alcohol and ether after an analysis has been completed.

For the preparation of the methyl magnesium iodide necessary to fill the 500-cc. reservoir we use the following procedure. In a one-liter three-necked, round-bottomed flask, equipped with motor stirrer, dropping funnel and condenser, are placed 12 g. of magnesium and 100 g. of isoamyl ether (distilled *in vacuo,* over sodium). In the course of one hour, with the temperature maintained below 20°, 60 g. of methyl iodide in 50 g. of isoamyl ether is added. Stirring is continued for two hours. The reagent is then diluted by the addition of 270 g. of isoamyl ether. The condenser is removed and the flask, immersed in an oil-bath, is heated at 120° for two hours; meanwhile a current of purified nitrogen is passed over the reaction mixture to carry away any readily volatile products. After being allowed to stand overnight, the reagent is transferred to the apparatus.

We have found it advantageous to substitute dehydrite for the phosphorus pentoxide in G, and to enlarge the overfiow bulb in the gas buret H to 50 cc.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

NOTE

Mannitol from Haplophyton Cimicidum.—During the course of an investigation of the reported insecticidal properties of the plant *Haplophyton Cimicidum*, mannitol was isolated and identified. The crude crystalline material, separating from the concentrated alcoholic extract of this plant, from which pure mannitol was obtained, represented approximately 0.75% of the weight of the plant on a dry basis. The substance was identified by means of its tribenzacetol and hexacetyl derivatives.

INSECTICIDE DIVISION OF THE
BUREAU OF CHEMISTRY AND SOILS
UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND

N. L. DRAKE
JOSEPH R. SPIES

RECEIVED JULY 3, 1930
PUBLISHED SEPTEMBER 5, 1930

COMMUNICATIONS TO THE EDITOR

AN X-RAY EXAMINATION OF THE HIGHER NORMAL PRIMARY ALCOHOLS

Sir:

X-ray examination of the higher normal primary alcohols reveals an interesting distinction between the odd and the even carbon chain series. As is usual with such long-chain compounds, the large crystal spacing increases linearly with increasing carbon content, and in the case of the higher alcohols, when crystallized from ethyl alcohol, the long crystal spacings for the odd alcohols lie on the upper Curve, I (Fig. 1), while those for the even alcohols (above C_{16}) lie on the lower Curve, II. The point of interest is, however, that below C_{16} the spacings of the even alcohols lie

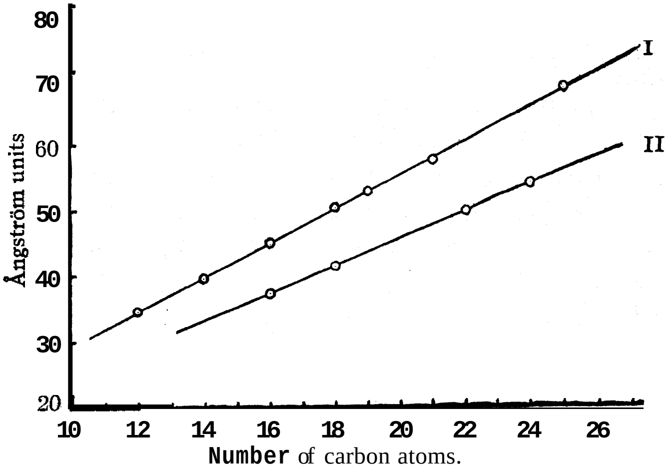

Fig. 1.

on the upper (odd) line, C_{16} alcohol itself gives two spacings, one on each line, while C_{18}, if fused, then gives a spacing on the upper line. The spacings of the odd alcohols, crystallized from solvents or fused, lie on the same upper line.

If the diameter of the carbon atom is taken as 1.54 Å., the spacings on Curve I correspond closely to a vertical chain of carbon atoms inclined tetrahedrally to each other, and those in Curve II to a similar chain tilted at an angle of 55° 40'. The vertical form is clearly a stable form for the odd alcohols and the tilted form for the even, but the latter change into the vertical form at some point below fusion. Apparently this change takes place considerably below the melting point since myristyl alcohol C_{14}, m. p. 38°, crystallized from alcohol, gives a spacing corresponding to the vertical form, and cetyl alcohol C_{16}, m. p. 49.0°, exhibits both spacings, thus indicating in the latter case that ordinary room temperature is near the transition point.

The following data were obtained using the Ka-rays of iron reflected from thin layers of the alcohols pressed or fused on a glass strip and mounted on a Müller spectrograph. The intensity distribution indicates that the alcohols crystallize in double molecules with the hydroxyl groups in juxtaposition.

X-RAY DATA FOR NORMAL PRIMARY ALCOHOLS

No. of carbon atoms	**12**	**14**	**16**	**18**	**19**	**21**	**22**	**24**	**25**
M. p., °C.........	**23.0**	**38.0**	**49.0**	**59.0**	**62.0**	**68.5**	**72.0**	76.5–77	**78.5**
Spacing, pressed layer, Å........	..	**39.7**	..	**41.35**	**52.75**	**57.4**	**49.95**	**54.0**	**68.5**
Spacing, melted, layer, Å........	**34.8**	..	**37.4** **44.9**	**50.2**	**52.8**	**56.9**	...	.....	..

It is hoped that these data will be of service to those working on the higher natural alcohols since x-ray analysis promises to afford a ready method of identification. In particular it should be useful in distinguishing between those higher alcohols of adjacent carbon content that are so difficult to identify by purely chemical means. In a subsequent paper it is hoped to give an account of the x-ray data for long-chain nitriles and iodides.

The writer wishes to express his thanks to Mr. S. H. Piper for his friendly interest in this work.

H. H. WILLS PHYSICS LABORATORY
AND THE CHEMISTRY DEPARTMENT
THE UNIVERSITY
BRISTOL, ENGLAND

T. MALKIN

RECEIVED AUGUST 4, 1930
PUBLISHED SEPTEMBER 5, 1930

THE METALLIC PRECIPITATION OF ZIRCONIUM

Sir:

The preparation of zirconium of a high degree of purity is not easy. The element combines or alloys itself with the reducing agents employed to prepare it. Probably the best method now used was devised by A. E. van Arkel and H. de Boer, who have obtained the metal by passing the vapor of the tetraiodide over a heated tungsten filament. Many metals may be prepared by precipitation from solution by a more electropositive substance than themselves. H. N. Warren[1] appears to have been the only one to employ this method for the preparation of zirconium. He states that if a rod of magnesium be wrapped with a few coils of asbestos paper and immersed in a solution of a metallic salt, the metal is precipitated on the asbestos in crystalline form. "Even zirconium was gradually reduced." This statement is erroneous, for zirconium compounds hydrolyze in water with the formation of free acid which would react with the magnesium.

It was thought, however, that zirconium might be precipitated from a solution other than aqueous. It was found that zirconium sulfate was quite soluble in methyl alcohol, the salt dissolving with a hissing sound and crystallizing out on evaporation. The alcoholic solution of zirconium sulfate was treated with metallic zinc. Hydrogen was given off, and the surface of the zinc was covered with a dark deposit. The reactions were accounted for by the equations

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2 \qquad (1)$$
$$2Zn + Zr(SO_4)_2 \longrightarrow 2ZnSO_4 + Zr \qquad (2)$$

Since all zirconium sulfate contains a small amount of free sulfuric acid, introduced by methods of manufacture and by hydrolysis, the presence of hydrogen may be accounted for by Equation 1. As the reaction continued, the amount of hydrogen evolved decreased until no more gas was given off. The acidity decreased proportionally until at this point it took as much as five minutes for blue litmus to turn red. When a part of the deposit was scraped off and treated with hydrochloric acid, the zinc removed along with the deposit dissolved, leaving undissolved zirconium on the bottom of the container.

When magnesium was substituted for zinc, a white precipitate of undetermined composition was formed and no zirconium was precipitated.

The inability to continue this study for some time has caused this preliminary report to be prepared

3950 WALNUT STREET
KANSAS CITY, MISSOURI
HOWARD S. GABLE

RECEIVED AUGUST 6, 1930
PUBLISHED SEPTEMBER 5, 1930

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[1] Warren, *Chem. News*, **61,** 183 (1890).

NEW BOOKS

The Condensed Chemical Dictionary. Compiled and edited by the Editorial Staff of the Chemical Engineering Catalog. FRANCIS M. TURNER, Editor. Second edition, completely revised and enlarged under supervision of THOMAS C. GREGORY, Editor, and ISABELLE M. WELCH, Assistant Editor. Book Department, The Chemical Catalog Co., Inc., 419 Fourth Avenue, at 29th Street, New York, U. S. A., 1930. 551 pp. 16 X 23.5 cm. Price, $10.00.

This book is essentially a list of useful chemical materials, the substances employed and produced in the chemical arts and industries, together with such information as formulas or compositions, colors, important properties, constants (d., b. p., m. p.), solubilities, derivations, grades, commercial containers, shipping regulations, fire hazards, etc. The cross indexing is unusually complete. The new edition contains some 12,000 titles as compared with about 7000 in the old. In spite of this very considerable increase in contents the volume is less bulky and more easily handled than the earlier one because of the use of thin paper and smaller type. The preferred usages of the American Chemical Society with regard to spellings and terminology are in general followed, although it is to be regretted that in this second edition as well as in the first, a few obsolescent forms such as sulfocyanide (for thiocyanate) are still used.

The book is especially valuable to the general chemist because of the inclusion of trade and proprietary names in great variety, in spite of the fact that a few common names (vitreosil, chromel, pyrex) for some reason do not appear in their respective alphabetical positions. The relationship of this volume to the bulky Chemical Engineering Catalog issued by the same publishers is close; and, although the general appeal of the Dictionary is to the industries, it furnishes much general information of interest to all chemists and not easily found elsewhere.

WILLIS A. BOUGHTON

L'Ancienne et la Nouvelle Théorie des Quanta. (The Old and New Quantum Theories.) By EUGÈNE BLOCH, Professor of Physics at the Sorbonne. Librairie Scientifique Hermann et Cie., 6, Rue de la Sorbonne, Paris, France, 1930. iii + 417 pp. Illustrated. 16.5 X 25 cm. Price, 90 fr.

This book, based on courses of lectures given by Professor Bloch at the Sorbonne in 1926–1927, 1927–1928 and 1928–1929, furnishes the most satisfactory introduction to the quantum theory that the reviewer has seen. It is elementary, in the very best sense of the word, in that it contains a clear, coherent and detailed discussion of the nature of the fundamental concepts of the old and new quantum theories, and presents simple and important examples of their application, without the burden of more complicated ones. It thus differs from those treatises which appear to contain a hodge-podge of everything the authors have ever heard about, unillumined by any clear understanding of the theoretical basis upon which they are presumably proceeding. It is written in a French which seems clear and beautiful even to one but meagerly acquainted with that language. Its translation into English to make it more widely available would seem eminently desirable.

After an introductory historical chapter which sketches the course of development both of the old and new theories, the first half of the book is devoted to the exposition of the old quantum theory, including a well-balanced correlation with experimental results. This part of the book also contains a useful chapter on fundamental results of analytical mechanics.

The second half of the book is devoted to the new quantum mechanics, and here the author's clear treatment of fundamental notions is in especially pleasing contrast to the work of minor scientists who hurry into print with the complicated applications of theories that they do not understand. The author first considers the waves of de Broglie and the actual experiments showing the wave character of the electron. This is followed by chapters on the wave mechanics of Schroedinger, and the matrix mechanics of Heisenberg, including a demonstration of their equivalence. Clear expression is given to modern ideas as to the principle of indeterminism, and the fundamental wave-particle duality in nature.

The transformation theory of Dirac and his treatment of the electromagnetic equations are not presented. The book concludes with a very good introduction to the new forms of statistical mechanics. It contains a fairly complete Table of Contents but no Index.

RICHARD C. TOLMAN

Chimica Farmaceutica e Tossicologica (Inorganica ed Organica). (Pharmaceutical and Toxicological Chemistry.) By BERNARDO ODDO, Professor at the University of Pavia. Casa Editrice, Dottor Francesco Villardi, Milan, Italy, 1930. Vol. I, vii + 486 pp. Vol. II, xii + 505 pp. Illustrated. 16.5 × 25 cm. Price, complete, lira 120.

This treatise is essentially a reproduction of the author's course of instruction in pharmaceutical and toxicological chemistry, including a brief exposition of the broader aspects of the subject. Departing entirely from the arbitrary custom of dividing the medico-pharmaceutical products into inorganic and organic groups, the author follows a pharmacological scheme of classification, treating the subject, in Vol. I, under the following heads: antiseptics, caustics, tonics and hematinics, purgatives, emetics, diuretics and uric acid solvents, vermifuges, vasodilators and -constrictors, while Vol. II is given over to antiseptics, anesthetics, sedatives, hypnotics, carbohydrates and artificial sweeteners, active principles of essential oils, alkaloids, glucosides, extractives, biological products, certain highly toxic principles and drug accessories. Throughout the entire work frequent reference is made to structural chemistry as related to pharmacological action for the proper evaluation of various synthetic drugs, in connection with the reasons for arriving at certain conclusions, and how it is possible to conceive and prepare new drugs to be tested pharmacologically. The treatise concludes with a chapter on toxicological analysis, in addition to a table of atomic weights, conversion tables and a comprehensive index.

W. O. EMERY

Die **Kolloide** in Biologie und **Medizin.** (Colloids in Biology and Medicine.) By Professor Dr. H. BECHHOLD, Director of the Institute for Colloid Research, Frankfort-on-Main. Fifth, revised edition. Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1929. xii + 586 pp. 87 figs. 16 X 23 cm. Price, unbound, RM. 32; bound, RM. 35.

In this fifth revised edition, Bechhold's well-known book has been brought up to date. The extent to which the author has mastered the increase in knowledge since the first edition appeared (1912) may be judged by the fact that the present edition, though greatly increased in scope, has almost been maintained in size within the limits of the first edition. This achievement may partly be ascribed to the nature of the recent developments in knowledge, many of which have replaced bulky empiricisms with concise theoretical formulations, partly to the splendidly critical sifting of material practised by the author. Any author who restricts his presentation to the most essential methods of a science which is in rapid development will inevitably stimulate discussion not only of the material included, but of that omitted.

The original subdivisions which proved so fruitful a means of presenting the vast material have remained unchanged. The first part of the book deals with the definitions and methods of colloid chemistry. Here considerable changes over the previous form have occurred and the author has brought the new material into the old plan without giving that feeling of lack of homogeneity which attaches to so many "revised" editions.

The second part is entitled "biocolloids." The main chapters are concerned with carbohydrates, lipoids, proteins, foodstuffs, enzymes and, as a new addition, immunity reactions. This chapter was written in collaboration with Dr. Laszlo Reiner. References to the current literature render these chapters extremely valuable, even though it be impossible to cover the immense field which might be comprised under the chapter heads.

Part three deals with the organism as a colloid system. In this part Bechhold has presented a great amount of histological, physiological and biological material from the point of view of the colloid chemist. To all those who are interested in medical science, this part, written with a profound knowledge of the problems involved, will be very stimulating. This is a clever selection of those fields in which the phenomena can at least be considered at this time.

Part four, finally, gives some of the applications of colloid chemistry to toxicology, pharmacology and microscopical technique. The very complete index, together with the references to the original literature, will be of great value to those who wish to follow the indicated problems.

For the sake of the reader with medical training, Bechhold has avoided, wherever it seemed possible, the use of mathematical formulas. It might be questioned if the medical reader ought not to be educated in the understanding of mathematical formulations through just such a book in which colloid chemistry is brought into contact with biology and medicine.

It may be concluded, I think, that the hope expressed by reviewer L. J. Henderson in these pages regarding the first edition, namely, "that this work will, through future editions, grow up with the subject" is in large part fulfilled by this new edition.

ALEXANDER VON MURALT

An Index to the Chemical Action of Microorganisms on *the* Non-Nitrogenous Organic Compounds. By ELLIS I. FULMER, Ph.D., Professor of Biophysical Chemistry, and C. H. WERKMAN, Ph.D., Associate Professor of Bacteriology, Iowa State College, assisted by Anella Wieben and Calvin R. Breden, Instructors in Chemistry, Iowa State College. Charles C. Thomas, Publisher, 220 East Monroe Street, Springfield, Illinois, 1930. xiii + 198 pp. 15.5 X 23 cm. Price, $4.50.

When we consider that there is probably no organic compound in nature that is not attacked by some microorganism, we must admire the courage of the authors in undertaking this index. They have delimited the field, however, by considering only "those instances in which a named organism acted on a named substance to produce a named compound." The material is arranged in three tables: Table I featuring the organisms, Table II the substrates and Table III the products. Each table includes the other two subjects and the references to the authorities cited—about 500 in number. The book contains much information in a compact and usable form. Every worker in the field of fermentation will want to have it on his desk for ready reference.

The chief criticism that must be made of the book is its incompleteness. While some subjects are treated rather fully, others are barely mentioned, or entirely neglected. No mention is made of the organisms which Conrad, Wehmer and Henneberg isolated from sauerkraut and to which they attribute the formation of this important food. In listing *Cl* acetobutylicum, the commercial butyl alcohol organism, the authors omit the paper on which the name is based. The fermentation of cellulose is dismissed with three references, while at least a half dozen important papers by Omelianski, Kellerman, et *al.*, Hutchinson and Clayton, Coolhaas, and Itano and Arkawa are omitted. The general occurrence of methane as a fermentation product in marshes, manure piles and the intestinal tract of animals would certainly entitle it to a place in the products table, but it is not listed, nor is Omelianski's organism, B. *methanigenes*, which produces it, given in the table of microörganisms. Two references are given to the formation of mannitol but the classic papers of Gayon and Dubourg, Van Steenberge and Miiller-Thurgau and Osterwalder are left unnoticed. The production of pyruvic acid and acetaldehyde by yeast is well indexed but some reference should also have been made to the equally important intermediate compounds, hexosephosphate and methyl glyoxal.

Some errors in the content of the tables have been noted. On page 73 it is said that propionic acid is formed by *Diplococcus pneumonia*. A careful reading of Brieger's original paper shows that not *Diplococcus pneumonia* but an unnamed short rod was the causal agent. The organism which is called B. *mobilis* on page 22 appears as B. *motilis* on page 84, and in the original paper by Orla-Jensen is given as B. *nobilis*. The reference, Mayer 1898, given in the tables does not appear among the references in the bibliography. Of forty references selected at random, sixteen contained more or less serious errors. The reviewer anticipates for the book a large demand which will call forth future editions and permit correction and expansion of its contents.

W. H. PETERSON

The Journal of the
American Chemical Society

VOL. 52 OCTOBER, 1930 No. 10

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

THE LINE SPECTRA OF IONS IN THE SOLID STATE IN THE VISIBLE AND ULTRAVIOLET REGIONS OF THE SPECTRUM. THE ABSORPTION SPECTRA OF $GdBr_3 \cdot 6H_2O$ AT ROOM TEMPERATURE AND AT THAT OF LIQUID AIR AND THEIR COMPARISON WITH THOSE OF $GdCl_3 \cdot 6H_2O$

BY SIMON FREED AND FRANK H. SPEDDING

RECEIVED MARCH 3, 1930 PUBLISHED OCTOBER 6, 1930

It is well known that the absorption spectra of the solutions of colored salts[1] consist of very broad bands and that the detail which the quantum theory requires to analyze them appears unattainable at present. The absorption spectra of crystals are less diffuse and they offer greater hope in this connection because the ions in a crystal lattice are subject to fields of greater regularity than exist in solution. It is a fact that the solutions of the rare earths possess relatively narrow bands and one would expect to find that their crystals would exhibit absorption spectra of exceptional sharpness.[2] In the next few paragraphs we shall attempt to show that the ions of the transition elements (the most common colored ions) should be regarded as polyatomic in the solid state and in solution, while those of the rare earths may be treated as atomic and hence as the simplest for spectroscopic study.

In his work on the spectra of complex atoms and ions in the gaseous state Hund[3] showed how to determine the character of the basic state of an atom (or atomic ion) from the number of the electrons in its various shells. He employed these basic states to calculate the magnetic moments of many ions but for lack of data upon paramagnetic monatomic gases he compared his results with the measured susceptibilities of ions in the solid state and in solution. The agreement was remarkably good in the case of the ions of the rare earths but there was no semblance of agreement with the ions of the iron group (the first long row of the periodic table). It seems then as if

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[1] Jones and Strong, *Carnegie Inst. Wash. Pub.*, No. 110 (1909); No. 130 (1911); No. 160 (1916).

[2] Bunsen, Pogg. *Ann.*, 128, 100 (1866).

[3] Hund, *Z. Physik*, 33, 853 (1925).

Hund's assumptions do not apply here and it is not difficult to find the reason.[4]

Let us compare a particular example of an ion in the iron group with one in the rare earth group, chromic ion and gadolinium ion. The electronic configurations of these ions in the gaseous state are electronic shells

	1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2
Cr^{+++}	2	2	6	2	6	3						
Gd^{+++}	2	2	6	2	6	10	2	6	10	7	2	6

We observe that the ions in the iron group have their incomplete electronic shells in the outermost orbits where they can readily couple with electrons of other substances such as Cl^- or H_2O. It is well known since the work of Werner that Cr^{+++} in solution is really $Cr(H_2O)_6^{+++}$. On the other hand, the unbalanced electrons in the structure of the ions of the rare earths are within the kernel of the ion and are shielded from external coupling by the completely filled 5_1 and 5_2 shells. In fact, the rare earths do not form complex ions and it is well known that their colors are unaffected (or only to a slight degree) by changing the medium in which they are dissolved. The ions of the iron group are extremely sensitive to their medium. For example, the addition of ammonia or cyanide ion completely transforms the colors of chromic ion or cupric ion. We conclude that there is a radical difference between the electronic configurations of these ions in the gaseous state and their configurations in solution. That is, chemical bonds between the water molecules and the metallic ion have transformed the atomic ion into a polyatomic or molecular ion and hence Hund's theory[3] for atomic ions is not applicable. We must have recourse to theories concerning the stationary states of polyatomic molecules, such as have been devised to interpret band spectra. Among the ions of the rare earths, no chemical coupling has occurred, so that these ions are truly atomic in solution and in the crystal. Their magnetic properties establish definitely that they have the same electronic configurations here that they have in the gaseous state. The water molecules are attached to the positive ions by the forces of electrostatic polarization and not by chemical bonds (pairs of electrons whose magnetic moments have neutralized each other).

According to this reasoning, the absorption spectra of the rare earths resemble the line spectra of monatomic gases, whereas the absorption spec-

[4] A great deal has been written upon the paramagnetism of the ions of the iron group. Many of the ions in solution and in the solid state display a paramagnetism which can be expressed readily in terms of the Bohr unit of magnetic moment, $eh/\pi m$ where e/m is the ratio of the charge divided by the mass of an electron and h is Planck's constant. This unit is employed constantly in the spectroscopic study of gases. Sommerfeld, "Atombau," Vieweg and Sohn, Braunschweig, 4th ed., 1924; Stoner. "Magnetism and Atomic Structure," E. P. Dutton and Co., New York, 1926; Freed, THIS JOURNAL, 49, 2456 (1927).

tra of the ions in the iron group resemble the band spectra of polyatomic molecules. We actually found in our work on the rare earths, especially in the case of gadolinium, that the absorption spectra consisted of very sharp lines.[5]

It should be remembered that the positive ion in the crystal lattice is constantly in the electric fields of its neighbors. At higher temperatures when the oscillations are more violent the variation in the intensity of the fields will be greater and consequently there is a greater variation in the energy levels of the positive ion which are affected by these fields. That is, different ions will be exposed to fields of different intensities and directions and consequently the light associated with these energy levels will vary slightly in frequency so that the resultant line observed will be broader at higher temperatures. A reduction in temperature will permit a refinement in the absorption spectrum. This influence of temperature was studied by Becquerel.[6]

When the oscillations in the crystal lattice have been so reduced that their effect upon the characteristic absorption is slight, it becomes possible to measure the influence of the size, charge and other properties of the neighbors of the positive ion upon its energy levels. So direct a quantitative study of the influence of one ion (for example) upon another is clearly of great chemical importance. Already vast stores of data have been accumulated showing the influence of chemical combination upon the x-ray energy levels of ions. The unit of energy employed in these investigations is so huge that the influence of chemical combination appears as a slight difference in large magnitudes. X-ray measurements are concerned with the energy necessary to remove an electron from a shell which has its full complement of electrons far inside the kernel of the ion. In the investigation being reported the electrons that are most easily affected by the negative ion come into play, that is, those in the incomplete 4_4 electronic shell. In the x-ray region the smallest detectable energy difference is roughly a thousand times as large as can be detected in the visible region of the spectrum. The quantitative correlation of such magnitudes as heats of solution, etc., with the energy levels of the spectra we are working with is within the range of reasonable expectation.

Experimental Methods **and** Results.—We are now reporting upon the absorption spectra of $GdBr_3 \cdot 6H_2O$ taken at room temperature and at that of liquid air. We also wish to indicate differences between these spectra and those of $GdCl_3 \cdot 6H_2O$ reported elsewhere.[5] For details as regards some of our apparatus and the method of growing single crystals we must refer to the paper[5] previously mentioned.

The crystals grow in colorless flat rhombohedra. The light was passed

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[5] Freed and Spedding, (a) Nature, 123, 525 (1929); (b) *Phys. Rev.*, 34, 945 (1929).

[6] J. Becquerel, Gedenkboek H. Kammerlingh Onnes. Leiden, 1922.

perpendicular to two parallel sides which did not require polishing. It has been known for a long time that the frequency of the light absorbed is the same along the different axes of a crystal. The intensities, however, may be different.[7]

The source of the continuous radiation in the ultraviolet was a hydrogen discharge tube with aluminum electrodes, as described by Bay and Steiner.[8] The spectrum was continuous and rather uniform in intensity down to 2000 Å.—the limit of our spectrograph.

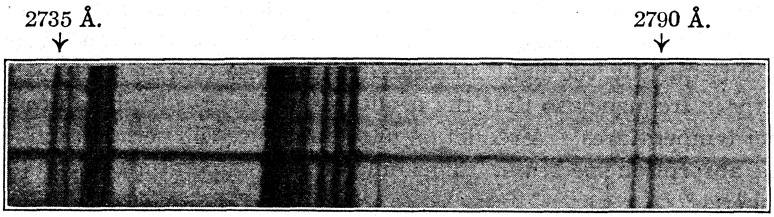

Fig. 1.—Absorption spectrum of $GdBr_3 \cdot 6H_2O$ at room temperature.

The absorption spectra of $GdBr_3 \cdot 6H_2O$ at room temperature were taken with a spectrograph having two quartz prisms with a dispersion of 3.5 Å. per mm. at 2350 Å. and 20 Å. per mm. at 4000 Å. This spectrograph was not available when the spectra at the temperature of liquid air were taken. The latter were photographed with a large Hilger spectrograph containing a single quartz prism. Its dispersion was 6 Å. per mm. at 2350 Å. and 34 Å. per mm. at 4000 Å.

The bromide is extremely hygroscopic and its handling was made easier by covering the crystal with a very thin layer of collodion, which was transparent in the spectral regions investigated.

It happened that the most satisfactory spectra of the bromide were obtained from a particular crystal about 0.8 mm. thick which originated from C. P. gadolinium oxalate procured from the Welsbach Company and twice reprecipitated and recrystallized. If any lines had appeared in the bromide which did not have their counterpart in the chloride, we should have been inclined to attribute them to slight impurities. (However, such was not the case.) Our chloride was made from a sulfate especially purified for us under the direction of Professor B. S. Hopkins of the University of Illinois, who was kind enough to give us also the following chemical history of the sulfate.

"Gadolinium material accumulated in this Laboratory (University of Illinois) from various rare earth sources was repeatedly precipitated as hydroxide by the addition of ammonia to a solution of the chlorides. The

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[7] Bunsen, *Pogg. Ann.*, **128**, 100 (1866); H. Becquerel, *Ann. chim. phys.*, 6, **170** (1888).

[8] Bay and Steiner, *Z. Physik*, **45**, 337 (1927).

mixture was then treated with hydrogen sulfide, filtered, and the rare earths in the filtrate were precipitated as oxalates with oxalic acid, ignited to the oxides, dissolved in hydrochloric acid, precipitated as hydroxides by ammonia, and finally converted to the nitrates by dissolving in nitric acid. Bismuth nitrate was added and the mixture was subjected to fractional crystallization of the simple nitrates in nitric acid solution. After prolonged fractionation, part of the material was precipitated as oxalate, ignited, and dissolved in nitric acid with the addition of sufficient magnesium oxide to form the double rare earth magnesium nitrate. This material was subjected to further fractional crystallization. All the gadolinium free from the other rare earths was then precipitated twice as oxalate to remove magnesium, then dissolved in hydrochloric acid and treated repeatedly with hydrogen sulfide to remove bismuth until no further precipitate of bismuth sulfide was obtained. The gadolinium was precipitated as oxalate, ignited, dissolved in nitric acid and fractionally crystallized five times as simple nitrate. The material was then precipitated as oxalate, ignited for twenty-four hours, and the oxide was suspended in a large volume of water to which sulfuric acid was added. The sulfate solution was evaporated slowly and the crystals were dried in an oven at 110°.

"The samarium present was estimated spectroscopically to be approximately 0.2%. No indication was observed of europium, while there was a possible trace of terbium, although no spectroscopic evidence of its presence was obtained. The sulfuric acid had the following limits of impurities (%)

HCl	*0.00005*	*Heavy metals*	*0.0005*
Fe	.00008	*Non-volatile*	.0006
As	.000001		

TABLE I

WAVE LENGTHS OF $GdBr_3 \cdot 6H_2O$ AND $GdCl_3 \cdot 6H_2O$

$GdBr_3 \cdot 6H_2O$				$GdCl_3 \cdot 6H_2O$					
Room temperature		Liquid air temperature		Room temperature		Liquid air temperature		Liquid hydrogen temperature	
(Å.)	(cm.$^{-1}$)	(Å.)	(cm.$^{-1}$)	(Å.)	(cm.$^{-1}$)	(Å.)	(cm.$^{-1}$)	(Å.)	(cm.$^{-1}$)
		4646.3	21516	4644.9	21523.0	4646.62	21515.0	4647.05	21513.0
		4154 7	24062[a]			4157.9	24044		
		4153 6	24069			4157.2	24048		
						4152 7	24074	4156.84	24036.5
						4152 3	24076	4153.28	24070.5
		4074 0	24539[b]			4073 7	24541		
		4073.5	24542			4072.7	24547	4074.11	24536.5
?		4029 0	24813	4026.6	24026	4026 2	24830		
		4028 5	24816	4024.5	24841	4024 8	24839	4025 75	24833.0
?		4012 5	24884	4016.4	24891	4014.1	24905	4014.10	24906.0
		4016.8	24888			4013.6	24908		
						4012 8	24913		
				4011.4	24922	4011.9	24919	4012 61	24914 5
3118.10	32061.5	3118.90	32053.5	3117 04	32072 5	3117 52	32067.5	3117.67	32066.0
3114.85	32095 0	3115 40	32089.5	3114.87	32094 0	3114.95	32094.0	3115.19	32091.5
3112.10	32123.5	3112.50	32119.0	3112.14	32123.0	3112.13	32123.0	3112.33	32121.0

TABLE I *(Concluded)*

Room temperature		Liquid air temperature		Room temperature		Liquid air temperature		Liquid hydrogen temperature	
(Å.)	$(cm.^{-1})$	(Å.)	$(cm.^{-1})$	(Å.)	$(cm.^{-1})$	(Å.)	$(cm.^{-1})$	(Å.)	$(cm.^{-1})$
3109.90	32146.0	3110.25	32142.5	3109.86	32146.5	3109.91	32146.0	3110.10	32144.0
3061.20	32657.5	3061.90	32650.0	3060.54	32664.5	3061.00	32659.5	3060.82	32661.5
3057.25	32699.5	3057.85	32693.0	3057.08	32701.5	3057.27	32699.5	3057.17	32700.5
3053.60	32738.5	3053.95	32735.0	3053.61	32738.5	3053.53	32739.5	3053.53	32739.5
2793.15	35791.5	2793.60	35785.5	2792.67	35796.5	2793.07	35792.5	2793.22	35790.5
2790.20	35829.0	2790.70	35823.0	2790.10	35830.5	2790.49	35825.5	2790.72	35822.5
2788.20	35850.0	2788.95	35845.5	2788.70	35848.5	2788.90	35845.5	2789.08	35843.5
2786.50	35876.5	2786.90	35873.0	2786.52	35876.5	2786.68	35874.5	2786.83	35872.5
?	?	2767.9	36118	?	?	2767.77	36119.5	2767.66	36121.0
2766.45	36137.0	2767.10	36128.0	2765.90	36144.0	2766.47	36136.5	2766.47	36136.5
?	?	2765.9	36144	2765.06	36155.0	2765.63	36147.5	2765.63	36147.5
2764.00	36169.0	2764.45	36163.0	2763.86	36170.5	2764.29	36165.0	2764.33	36164.5
2762.85	36184.0	2763.35	36177.5	2762.65	36186.5	2763.07	36181.0	2763.10	36180.5
2761.60	36200.5	2762.05	26194.5	2761.62	36200.0	2761.88	36196.5	2761.92	36196.0
2760.45	36215.0	2761 20	36205.5	2760.93	36209.0	2761.23	36205.0	2761.31	36204.0
2759.95	36222.0	2760.15	36219.0	2759.86	36223.0	2760.17	36219.0	2760.09	36220.0
2759.40	36229.0			2759.08	36234.5	2759.37	36229.5	2759.40	36229.0
2758.85	36236.5		[c]	2758.53	36240.5	2758.87	36236.0	2758.83	36236.5
2758.30	36243.5			2758.11	36246.0	2758.46	36241.5	2758.42	36242.0
2757.85	36249.5			2757.66	36252.0	2758.03	36247.0[e]	2758.00	36247.5
2757.45	36255.0			2757.20	36258.0	2757.62	36252.5	2757.62	36252.5
2756.80	36263.0	2757.15	36258.5	2756.59	36266.0	2756.93	36261.5	2756.85	36262.5
?	?	2747.75	36382.5	2745.05	36418.5	2745.57	36411.5	2745.46	36413.0
2745.60	36411.5	2746.25	36402.5			2744.71	36423.0	2744.33	36428.0
?	?	2744.85	36421.0	2743.09	36444.5	2743.54	36438.5	2743.31	36441.5
2743.30	36442.0	2743.65	36437.0			2742.45	36453.0	2742.37	36454.0
2742.15	36457.0	2742.40	36452.0	2741.81	36461.5	2742.03	36458.5	2742.00	36459.0
2741.55	36463.5	2742.05	36458.0			2741.02	36472.0	2741.05	36471.5
2739.95	36486.5	2740.20	36483.0					2740.45	36479.5
2738.75	36502.0	2739.05	36498.0	2739.85	36487.5	2740.19	36483.0	2740.08	36484.5
2736.75	36529.0	2738.10	36511.0					2739.48	36492.5
2735.20	36551.0	2737.30	36521.5	2738.69	36503.0	2738.95	36499.6	2738.76	36502.0
2734.35	36561.0	2735.50	36545.5[d]	2737.12	36524.0	2737.83	36514.5	2737.94	36513.0
2733.65	36570.5	2734.05	36565.0	2735.80	36541.5	2736.33	36534.5	2736.26	36535.5
2732.90	36580.5	2733.20	36576.5					2735.36	36547.5
2731.90	36593.5	2732.30	36588.5	2734.68	36556.5	2735.06	36551.5	2734.95	36553.0
2731.15	36603.5	2731.25	36602.5	2734.12	36564.0	2734.38	36560.5"		
2730.80	36608.5					2733.75	36569.0		
2730.30	36615.5	2730.05	36618.5	2732.70	36583.0	2733.11	36577.5	**Unresolved** band	
2729.70	36623.2			2731.73	36596.0	2732.18	36590.0	**due to structure**	
2729.10	36631.0	2729.30	36628.5			2731.17	36603.5	in **source**	
						2730.24	36616.0		
				2726.84	36637.5	2729.31	36628.5	2728.78	36635.5
2727.80	36648.5	2727.85	36648.0	2727.48	36653.0	2727.82	36648.5	2727.79	36649.0
2727.00	36659.5	2727.05	36658.5	2726.85	36661.5	2727.07	36658.5	2727.0	36659.5
2530.35	39508.5	2530.50	39506.0	2530.05	39513.0	2530.30	39509.0		
2529.40	39523.5	2529.55	39520.5	2528.90	39531.0	2529.10	30528.0		
2527.10	39559.0	2527.15	39558.5	2526.40	39570.0	2526.60	39576.0		
2525.25	39588.0	2525.20	39589.0	2524.70	39597.0	2524.85	39594.5		
2523.20	39620.5	2523.25	39619.5	2522.50	39631.0	2522.70	39628.5		
2464.00	40572.0	2464.00 f	40572.5	2463.15	40586.0	2463.25	40584.5		
2463.05	40588.0	2463.20	40585.5	2462.30	40601.0	2462.35	40599.0		
2446.75	40858.0	2446.90	40855.5	2446.10	40868.0	2446.50	40862.5		
2441.75	40941.5	2441.85	40940.0	2441.25	40950.0	2441.35	40948.0		

[a] Looks like two lines. Very faint band. [b] Very faint band, looks like two lines. [c] Band unresolved due to smaller dispersion. [d] Barely resolved due to small dispersion. [e] Not completely resolved due to smaller dispersion. [f] Background so faint lines difficult to measure.

Discussion of Results.—The absorption spectra even at room temperature consisted of extremely sharp lines, as may be seen from the photograph and the precision with which the frequencies could be determined (see table). The spectra lay almost entirely in the ultraviolet region except for a few faint diffuse lines in the visible. These lines became markedly finer at the temperature of liquid air.

The magnetic measurements of Kammerlingh Onnes and his associates[9] show that the magnetic behavior of Gd^{+++} in the solid state conforms with that expected theoretically from a "perfect magnetic" gas throughout the entire temperature range, from room temperature to 1.3°K. This "gas" (Gd^{+++}) consists of a single species having ^8S for its basic electronic level.[10]

It follows that the other electronic levels are rather far removed in terms of energy from the ^8S, for, otherwise, the ions having the electronic configurations corresponding to these levels would have contributed to the measured susceptibility and produced deviations from the theoretical curve. The latter had assumed that only one species was present.

The Hund theory predicts that other electronic levels belonging to systems of lower multiplicity than ^8S originate from the seven 4_4 electrons of Gd^{+++}. They correspond to different relative orientations of the spin and orbital moments of the seven equivalent electrons. Goudsmit[11] has shown that the relativity doublet separation given by the formula of Sommerfeld employed in the x-ray region of the spectrum

$$\Delta\nu = \frac{R\left(\frac{2\pi e^2}{hc}\right)^2 (Z-\sigma)^4}{n^3 l(l+1)}$$

can often be applied in the optical region to such electronic configurations in order to obtain the separations between the multiplets. Av is the difference in frequency between the doublet levels, R is Rydberg's constant, e is the charge of the electron, h is Planck's constant, c is the velocity of light, Z is the atomic number of the atom, σ is the screening constant derived from x-ray measurements, n is the total quantum number of the electron and l is its orbital quantum number. The separations expected in the rare earths are of the order of magnitude found between the groups of the Gd^{+++} spectrum. It appears probable even at this early stage of study that each group of lines would be a single line (if the ion were gaseous) corresponding to a transition from the basic level to a multiplet level and that this single line has been decomposed into a group of lines by the electric fields within the crystal. However, some of the levels have not been

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[9] Woltjer and Kammerlingh Onnes, Leiden Comm. No. 167C.

[10] (a) Hund, Z. *Physik,* 33, 853 (1925); (b) Giauque, THIS JOURNAL, 49, 1870 (1927).

[11] Goudsmit. *Phys. Rev.*.31, 946 (1928).

decomposed into their maximum number of components. We have already found from spectroscopic measurements in a magnetic field (Zeeman Effect on Solids) that further decomposition of some of the lines (or levels) can be effected.[12]

It is easy to tabulate many of the lines of the Gd^{+++} spectrum into multiplets having constant energy differences. Such a tabulation need not lead to unique energy levels even in the spectra of gases unless further information such as is furnished by the study of the Zeeman Effect, etc., is available. It is with the aim of getting unique energy relations that our work on the Zeeman Effect in crystals is being undertaken.

We have also made polarization spectra (which we shall publish later together with the work on the Zeeman Effect) which show that the lines are polarized in relatively different directions. Such a behavior cannot be attributed to any crystalline dissymmetry, for then all the lines would be polarized more or less uniformly.

It is characteristic of the Stark Effect, that is, the interaction of an electric field with radiant matter, that it produces lines which are polarized. The polarization of the spectral lines definitely expresses the electrical influence of the neighbors of the positive ion upon its spectrum. The identification of the polarization of the lines with that observed in the Stark Effect on gases is the same as the interpretation previously advanced[13] that the polarization discloses the regular orientation of the observing ions by the crystalline forces. In the Stark Effect the external field brings about an orientation or a quantization of the ion with respect to the direction of the field and then the transitions between the resultant states of the ion give rise to light which is polarized.

The astonishing sharpness of the lines in the spectrum of Gd^{+++} even at room temperature shows that the Gd^{+++} is not sensitive to the variation in the perturbing action of the external electric fields. One would expect 'that the thermal oscillation of the constituents in the crystal lattice would produce a great broadening, for example, such as is found in Sm^{+++}, Er^{+++}[14] at room temperature. The shielding of the 4_4 electrons by the complete shells of the 5_1 and 5_2 electrons is particularly effective in Gd^{+++}. As has been previously mentioned, the basic level of Gd^{+++} is an ^8S which implies that the orbital momenta of all seven electrons in the 44 shell have completely neutralized each other. Such a neutralization leads to a distribution of electron density having spherical symmetry, according to the quantum mechanics; that is, the electrons are probably grouped compactly inside the shielding 5_1 and 5_2 shells of electricity. In the language of

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[12] Becquerel (Ref. 6) in studying the influence of a magnetic field upon the polarization of the light absorbed by his substances observed a splitting of some of the lines.

[13] Brunetti, *Physik. Z.*, 29, 571 (1928).

[14] Freed and Spedding, *Nature*, 123, 525 (1929).

orbits, we may say that the average time in which the 4_4 electrons are close to the perturbing agents is slight. In the less symmetrical electron distributions which exist among ions such as Eu^{+++} or Sm^{+++}, the eccentricity of their orbits implies that the electrons are very close to the sources of perturbation a considerable fraction of the time. Hence their energy levels are capable of great variation since they accompany the oscillations of the perturbing agents. Their spectral lines are more diffuse.

So symmetrical an arrangement of the seven electrons leads to a coupling of great stability. That is, the energy level corresponding to this coupling is considerably lower than any other (a sort of maximum stability). It is probable that the nearest energy level to which any rearrangement would correspond is so far above its basic level that ultraviolet light is necessary for any transition. (In other words, it would be surprising if any transitions could be brought about in absorption by means of infra-red radiation. If it occurs it would probably be faint and due to a transition from an activated level. We are inclined to believe that the faint diffuse lines in the visible are of a similar origin. Their very diffuseness suggests that the transition begins at an electronic state of less stability than the basic ^8S.)

At the low temperature, there is a general readjustment of the energy levels so that the lines shift slightly toward the longer wave length regions of the spectrum. This change (already discussed in our communication on $GdCl_3 \cdot 6H_2O$) may be attributed to the thermal contraction of the crystal. The constituents of the crystal are on an average nearer each other at the lower temperature and the closer approach of a bromide ion, for example, has probably shifted the outer energy level (corresponding to the activated state of Gd^{+++}) more than the inner. That is, the energy levels have approached each other (in terms of energy) and a transition between them corresponds to a smaller change in energy than at the higher temperature. The light is of longer wave length.

Comparison of Spectra of $GdBr_3 \cdot 6H_2O$ and $GdCl_3 \cdot 6H_2O$.—There appears to be a complete parallelism among the spectra of the bromide and the chloride, that is, a line for line correspondence in their spectra. It is fairly certain from analogies with salts of similar composition that the six molecules of water are grouped more or less symmetrically about the gadolinium ion. Hence any difference in the spectra of $GdCl_3 \cdot 6H_2O$ and $GdBr_3 \cdot 6H_2O$ can be ascribed to a first approximation to the difference in character between the bromide ion and the chloride ion. The results show that the corresponding lines in the two spectra are very nearly the same, a fact in keeping with the supposition that the molecules of water are between the negative ions and the gadolinium ion. The spectra indicate that the bromide ion induces a slight approach in the gross energy levels (that is, the hypothetically "unsplit" energy levels) of the gadolinium ion, as follows from the general displacement of the lines toward longer wave lengths as compared with the corresponding chloride lines. The bromide ion also brings about a slightly greater separation (on the average) between the lines comprising a group. We have attributed the existence of these groups to the electric fields surrounding the gadolinium ion (fields presumably arising principally from the polarized water molecules). Upon this basis, the displacement toward the red and the greater separation induced by the bromide ion can be related to the well-known deformability of the bromide ion, which would produce a greater negative charge upon the surface opposite the gadolinium ion than would the chloride ion.

Summary

We have discussed the possibility of applying the quantum theory of the line spectra of gases to ions in the solid state. We have concluded that the ions of the rare earths exhibit line spectra comparable with those of atomic ions in the gaseous state under the influence of external electric fields.

The absorption spectra of the crystal $GdBr_3\cdot 6H_2O$ were taken at room temperature and at that of liquid air. Its spectra even at room temperature consist of lines of extreme sharpness comparable with the lines of the iron arc which were used for comparison. The spectra lie almost entirely in the ultraviolet. There are a few faint diffuse lines in the visible.

At the temperature of liquid air there is a slight shift of the lines toward longer wave lengths and a greater separation between lines comprising each group. These displacements can be related to the thermal contraction of the crystal which brings the constituents of the crystal closer together. The fields due to the neighbors of the Gd^{+++} become then more intense than at the greater average distance at higher temperatures. The few diffuse lines in the visible become narrower and sharper at the temperature of liquid air. The spectra consist of groups of lines and these groups are separated by rather large intervals. We have regarded each group as corresponding to one line of the spectrum of Gd^{+++} ions in the gaseous state. This line has been decomposed into several lines by the electric fields arising from the neighbors of the Gd^{+++} ions in the crystal lattice.

Some of the potentialities of such investigations are sketched. The influence of bromide ion upon the positive ion is roughly compared with that of chloride ion (a preliminary communication on the spectra of $GdCl_3\cdot 6H_2O$ was published in Phys. *Rev.*, **34, 945 (1929))** and this difference is related to the greater deformability of the bromide ion.

We are continuing and extending the study of the spectra of the ions of the rare earths with the hope of obtaining unique energy levels.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 63]

THE ROLE OF THE LIQUID STATIONARY FILM IN BATCH ABSORPTIONS OF GASES. I. ABSORPTIONS INVOLVING NO IRREVERSIBLE CHEMICAL REACTIONS[1]

BY HAROLD S. DAVIS[2] AND GEORGE S. CRANDALL[3]

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In the studies on the rates of absorption of olefinic gases by sulfuric acid which were reported in a previous communication[4] it was noted that the specific absorption coefficient (cc. of gas absorbed per sec. per sq. cm. of surface) was not appreciably affected by agitation of the acid. However, in the absorption chamber used (a horizontal cylinder) stirring was obtained by rotation, which also changed the area of the liquid surface exposed. Accordingly a new apparatus (described below) has been devised in which gases can be absorbed at various pressures by liquids with a constant area of surface exposed, while a stirrer is operating at a controllable speed beneath the liquid surface.

The results with the new apparatus have confirmed and extended the generalizations made from the former measurements with the rotating absorber. Some of the facts are at first sight surprising, *e.* g., that ethylene was absorbed by concentrated sulfuric acid as rapidly when the acid was quiescent as when it was stirred (without breaking the surface or changing its area) at 400 r. p. m. The writers have found that the various phenomena encountered are best explained in terms of the so-called "two film theory" of gas absorption. For this purpose it has been necessary to study and extend further by experimental tests this important hypothesis.

"It is now becoming generally recognized that whenever a liquid and a gas come in contact there exists on the gas side of the interface a layer of gas in which motion by convection is slight compared to that in the main body of the gas and that similarly on the liquid side of the interface there is a surface layer of liquid which is practically free from mixing by convection. This phenomenon is frequently expressed by assuming the existence of stationary films of gas and liquid on the two sides of the interface."[5]

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[1] This paper contains results obtained in an investigation on the "Relative Rates of Reaction of the Olefins," listed as Project No. 19 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] Director and Research Associate, Project No. 19.

[3] Junior Research Fellow, Project No. 19.

[4] Davis and Schuler, THIS JOURNAL, 52, 721 (1930).

[5] Lewis and Whitman, *Ind.* Eng. Chem.. 16, 1215 (1924).

There is good evidence that a similar liquid stationary film exists at a liquid–solid interface. Noyes and Whitney[6] showed that the rate of solution of a solid in water is proportional to the difference between the saturation concentration and its concentration in the water. They assumed that at the interface between the crystals and the liquid the solution is at each moment saturated. The velocity of solution according to this is conditioned only by the rate of diffusion through an unstirred layer close to the solid. Brunner[7] in a very important research extended this work and measured rates of solution per unit area of interface. Nernst[8] suggested that this hypothesis can be so generalized as to apply to all reactions in heterogeneous systems. The similarity of the phenomena caused by the liquid stationary films at various types of interfaces (liquid–gas, liquid–liquid and liquid–solid) should be emphasized.

This paper will be limited to consideration of the role of the liquid stationary film in determining the rates of gas absorption where no irreversible reactions are involved. When dealing with a pure gas of moderate solubility, the effect of the gas film is negligible.

Lewis and Whitman[5] state, "Resistance to diffusion due to the gas film is, of course, non-existent in the special case where an absolutely pure gas is being absorbed. This problem is very rarely encountered in practice, however, since the presence of very small amounts of inert gas which will concentrate at the liquid surface is sufficient to create an effective gas film." This statement might imply that the inert gas is adsorbed on the surface of the liquid and forms a gas film, even at equilibrium conditions, in which its concentration is greater than in the main body of the gas. To such a conception H S. Taylor[9] has objected that, "It is not in harmony with so much of the treatment found valid by Langmuir in the case of reactions at solid surfaces. On Langmuir's method of treatment there should be no gas film of the nature postulated by Whitman. A unimolecular layer of adsorbed molecules would represent the maximum film which could be formed."

However, it would appear that the fundamental assumption made by Whitman is that on either side of the liquid–gas interface there exists a film of relatively quiet fluid and the gas being absorbed must pass through these films by diffusion. From these postulates Hanks and McAdams[10] have shown that a gas film of the inert gas must exist at the interface when the solute gas is being absorbed from the main body of the gas into the liquid. For, since the solute gas passes inward through the stationary gas layer, by diffusion, it must form a gradient of decreasing concentration to the liquid surface, and since the total gas pressure of inert and solute gas remains constant, there must exist a similar gradient of the inert gas outward.

The stationary films are by no means monomolecular in thickness, nor must they be confused with adsorbed layers. They are much thicker. Thus for water stirred underneath at 1000 r. p. m. the effective thickness is about 0.0045 cm.,[5] which is over a hundred thousand times the diameter of the water molecule.

The reality of the liquid stationary film is confirmed by common-place observations. Thus, dust particles often remain motionless on the surface of water in a well-stirred thermostat. The phenomena stand out still more

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[6] Noyes and Whitney, *Z. physik. Chem.*, 23, 689 (1897).

[7] Brunner, *ibid.*, 47, 56 (1904).

[8] Nernst, *ibid.*, 47, 52 (1904).

[9] Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1926, p. 1001.

[10] Hanks and McAdams, *Ind. Eng. Chem.*, 21, 1034 (1929).

plainly under the microscope in water containing fine particles, *e. g.*, freshly precipitated barium sulfate. The solid particles at the surface *and also* for *a short distance beneath it* appear to be in a separate medium of their own which slips along the water like a thin skin. A little deeper down, the particles are carried here and there by currents and move past the outlines of those at the surface like low-lying storm clouds against those high in the sky.

The writers determined the distance between the quiet particles on the surface and those moving freely beneath it, under a microscope at about 50 diameters magnification. The value obtained for quiescent water at room temperature, 0.04 cm., was checked with surprising closeness by different observers.

What causes the liquid "stationary" film? Some of the contributory factors can be pictured. Thus the upward motion of water in currents must cease before the surface is reached. Again, local currents across the surface are opposed by some force, perhaps that of surface tension. This is indicated by the tendency to preserve their relative spacing shown by particles lying on the surface. It is significant that the effective thickness of the liquid stationary film at the gas–liquid interface is of the same order as that of the liquid film at a liquid-solid interface (see Table I, Note b).

Whatever the causes of its existence, the liquid stationary film plays a major role in the absorption into or the evolution of gases from liquids. With moderate stirring, the main body of the liquid and the main body of the gas are each practically uniform in composition and the gas must pass from one phase to the other through the unstirred layers at the interface mainly by diffusion. In another communication it will be shown that where irreversible chemical reactions are involved, the whole reaction often takes place in the liquid stationary film and the gas never reaches the main body of the liquid at all.

When a pure gas, oxygen for example, is suddenly admitted at atmospheric pressure into contact with pure water from which all gases have been removed, the very surface layer, perhaps monomolecular in thickness, instantaneously becomes very nearly saturated with oxygen.[8] This must be true, because an oxygen pressure is at once exerted from the surface equal to the partial pressure against it, which is the condition necessary for a saturated solution.

The oxygen now begins to diffuse into the film at a tremendous rate, for although the solubility of oxygen in water is small, 0.0012 M, the gradient from the surface is very steep. We wish to stress this point because of its bearing on the rapid rates at which some olefinic gases are absorbed by sulfuric acid, although they are quite insoluble therein.

As diffusion proceeds the magnitude of this gradient quickly grows less and the absorption slows down, soon reaching a constant value *(initial absorption rate).* At this stage the gradient is uniform and the same quantity of oxygen is passed from the surface through each unit cross section of the film into the main body of the liquid which is still practically free from dissolved oxygen.

The Time Required to Build up an Oxygen Gradient through the Film of Water.—Table **I** shows that the time necessary to establish a uniform gradient through the stationary liquid film depends on the degree of agitation in the water. It can be practically established (98%) through the sides of bubbles in one-tenth of a second, whereas five seconds are required in the case of moderately stirred (60 r. p. m.) water and in the case of quiescent water a still longer period is needed since here an effective film thickness of several millimeters is sometimes encountered.

These conclusions are substantiated by the measurements of Monaweck and Baker[11] on the rates of absorption of pure ammonia gas by water. With stirring at 324 r. p. m., no high initial absorption was noted (readings being taken every ten seconds) and the rate remained constant for 110 sec. Evidently a uniform concentration gradient was very rapidly established through the **film.** Further, calculation shows that $k_L = 1.3 \times 10^{-6}$ for these experiments, which is in good agreement with a value 2.2×10^{-6} found by the writers from measurements of the absorption rate of carbon dioxide, a much less soluble gas, by water under similar conditions.

On the other hand they found that the absorption rate of pure ammonia by quiescent water fell off over a period of 100 seconds to less than one-sixth of its initial value.

TABLE I

SHOWING THE RISE OF THE CONCENTRATION WITH TIME IN THE CENTER OF THE LIQUID STATIONARY FILM DURING THE ABSORPTION OF OXYGEN BY WATER EXPRESSED AS PERCENTAGE OF THE VALUE AT UNIFORM ABSORPTION (= 0.5 SURFACE CONCENTRATION)[a]

Absorption conditions	*Thickness of film,[b] cm.*	Seconds					
		001	0.1	0.2	0.5	10	5
Water stirred at 60 r. p. m.	0 020	..	..	..	..	20%	88%
Water stirred at 1000 r. p. m.	0045	..	50%	80%	99%	..	..
Bubbles in water	0021	18%	98%	..	..	..	..

[a] In these calculations it has been assumed that the inner limit of the stationary film is sharply defined and that the concentration of dissolved oxygen at the interface, C_i, remains constant (saturation value), while that at the inner edge and in the main body of the solution can be regarded as zero.

It is further assumed that the course of the oxygen diffusion at all times satisfies the equation $\partial c/\partial t = \Delta(\partial^2 c/\partial x^2)$, (see, however, Lewis and Chang, ***Trans. Am. Inst. Chem. Eng., 21,*** 135 (1928)), where c is concn. of dissolved oxygen, moles per liter; t is time in seconds after oxygen comes into contact with the deoxygenated water; x is distance in cm. from the surface; A is diffusion coefficient for oxygen through water.

The writers are indebted to Professor F. C. Hitchcock for a solution of the &fferential equation for these conditions in terms of a Fourier series.

[b] These values are taken from the calculations of Lewis and Whitman except for

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[11] Monaweck and Baker, ***Trans. Am. Inst. Chem. Eng., 22,*** 165 (1929).

that for bubbles in water, which was calculated by the writers from the data of Adeney and Becker discussed below.

It is interesting to compare these values for the thickness of the liquid stationary film at a gas–liquid (water) interface with those obtained by Brunner, Z. *physik. Chem.*, 47, 99 (1904), for the liquid stationary films at the surface of solids in well-stirred liquids—0.0030 cm. for pure water and 0.0028 to 0.005 cm. for various solutions.

Experimental

The absorption apparatus was designed to operate at atmospheric pressure or at any desired reduced pressure. Accordingly it was necessary that the seal around the stirrer should stand high vacua, so that an ordinary mercury ring seal could not be used.

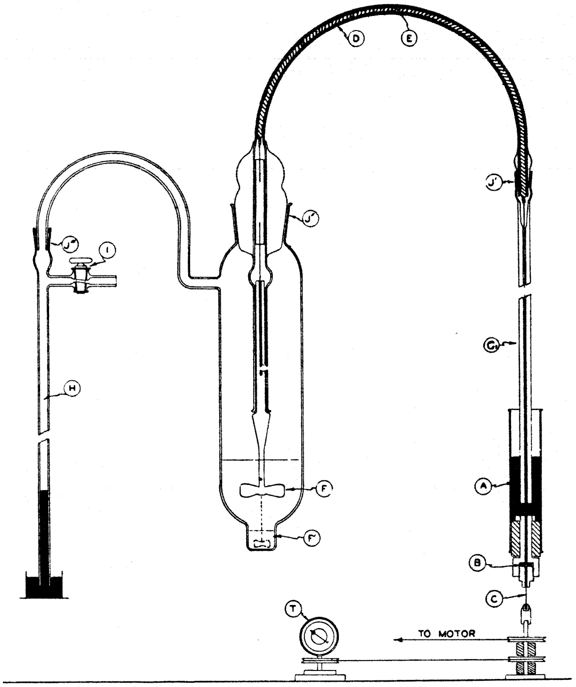

Fig. 1.—Diagram of apparatus for gas absorptions by liquids at atmospheric or at reduced pressures. **A,** mercury seal; B, packed joint through which drive shaft (C) passes upward through capillary tube (C_1); D, semicircular arc of glass tubing containing a flexible rope pattern watch chain; E, which transmits power to stirrer, F; $J^1J^2J^3$, ground-glass joints; H, manometer tube; T, tachometer calibrated to register r. p. m. of stirrer.

The main outline of the apparatus will be plain from the figure. Its unique feature is the manner in which the stirrer is operated. The mercury seal **(A)** is outside the apparatus at the bottom of the vertical capillary tube *(C)* which is longer than barometric height. The drive shaft (C) passes through a packed joint (B) in the bottom of the mercury cup, and extends to the top of the capillary tube. Thence the power is transmitted around the semicircular arc (D) by means of the flexible gold-filled, rope-pattern chain (E) to the stirrer proper (F) in the reaction chamber. The latter is suspended in a constant temperature bath.

Experiments at Constant Volume.—In the experiments a measured volume of the liquid was introduced into the bottom of the chamber by means of a long-stemmed funnel. The apparatus was then closed and evacuated through the side tube I. Next the gas was drawn in. The rate of absorption was followed by the change of pressure with time.

Suitable corrections were made for the changes in volume due to the rise of the mercury level in the drive tube and in the manometer tube.[12]

Experiments at Constant Pressures.—These were carried out with mercury-filled gas burets connected to the reaction chamber at I. In order to keep the gas pressure constant, the leveling bulb was slowly raised by means of a windlass and reducing gears whose speed could be suitably varied to correspond to the rate of absorption. Readings of the buret were taken with time. In the absorptions of olefins by sulfuric acid, in order to observe the rate when the quantity of olefin absorbed was 10% or more equivalent to the acid, two micro experiments were performed, using 1 cc. of acid. The regular stirrer was replaced by a smaller one which stirred the liquid in the small chamber without changing its surface.

The characteristics of the absorption chamber were as follows

Volume including connecting tubes[a] = 340.4 cc.

Area of liquid surface with 30-100 cc. of liquid[b] = 17 sq. cm.

Area of liquid surface in lower cup used for micro experiments (1 to 3 cc. of liquid)" = 1.41 sq. cm.

[a] Determined by change of pressure caused by addition of known volumes of air.

[b] Determined by adding known volumes of liquid and noting the rise in liquid level.

[c] Determined as in (b) except that the curvature of the meniscus had to be taken into account.

TABLE OF NOMENCLATURE

N = gram moles of gas
t = time in seconds
dN/Adt = rate of gas absorption per unit area of liquid surface—moles per sec. per sq. cm.

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[12] $P = (I - R) - 8$, where $8 = (B - R)AR/V_0$
P = Pressure of gas at time t corrected to V_0
I = Initial manometer reading before introduction of gas
R = Manometer reading at time t
B = Barometric pressure (uncorrected)
A = Sum of the cross sectional areas of the mercury in the manometer and drive-shaft tubes
V_0 = Volume of gas space in apparatus at atmospheric pressure

$(dN)/(A\,dt)_{\text{Init.}}$ = initial rate of absorption after practically stationary concentration gradients have been established in the liquid film, moles per square centimeter per second

A = area of liquid–gas interface in sq. cm.

k_L = a constant which, according to the theory outlined above, is equal to the diffusion coefficient of the dissolved gas through the liquid stationary film, that is, the number of moles which would diffuse through 1 sq. cm. of cross section in one second if the difference in the concentrations of the dissolved gas at the interface and in the main body of the solution were molar

C_i = saturation concentration of the dissolved gas in moles per liter at its partial pressure during the absorption

C_L = molal concentration of dissolved gas in the main body of the liquid at time t

C_S = concentration, moles per liter, of the reacting solute in the main body of the solution. (See paper II in this series)

Cof. = cc. of gas absorbed per sec. per sq. cm. of surface, measured at its own partial pressure.

To avoid confusion the C used in a former communication to denote gas absorption rate is here replaced by *Cof.* The other symbols are similar to those of Lewis and Whitman except that gas quantities and concentrations are expressed in gram moles rather than in grams.

Table II gives collected data on the initial rates of solution of oxygen and a few other gases by liquids under different absorption conditions. Direct comparisons are possible because in each case the investigators have measured the area of the gas–liquid interface so that the absorption rate per unit area could be calculated. The absorption methods were as follows.

I. Liquids at Rest and Liquids Stirred without their Surfaces Being Broken.—The writers have measured the rates of solution of oxygen and of carbon dioxide by water and of oxygen by tetrachloroethane in the apparatus which is described above. Measurements were carried out both at constant volume and at constant pressure (area of gas–liquid interface 17 sq. cm.).

Becker measured the absorption rate of oxygen from air[13] at constant volume by water containing suspensions of ferrous hydroxide precipitated directly therein from ferrous sulfate and potassium hydroxide; volume of liquid, 100 cc.; Area of surface except at high stirring, 11 sq. cm.

II. Gas Bubbles in Liquids.—Adeney and Becker[14] measured the

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[13] Becker, *Phil. Mag.*, 45, 681 (1923).

[14] Adeney and Becker, *ibid.*, 38, 317–337 (1919); 39, 385–404 (1920). The mathematical calculations of these investigators appear to contain certain errors which are confusing to the reader although they do not vitiate the important experimental data or the main conclusions. Thus they define "ω" as the "weight of gas per cc. in the upper layer" of liquid (cc. of gas instead of g. are given in their tables). However, they multiply its rate of change with time $d\omega/dt$ by V, the total volume of the liquid. in order to obtain the total rate of gas absorption. Evidently this latter relationship can only be true if ω represents the average concentration of the gas in the whole liquid. In Tables 1, 2, 3 and 4 of the first paper and Table 6 of the second, "w" and "a" should be "ωV" and "aV," respectively.

TABLE II
EXPERIMENTAL DATA

No.	Observer	Method of absorption	Gas	Temp., °C.	C_i, M	$\frac{(dN)}{(Adt)}$ Init.	k_L
		I. Stirred liquids					
1	Davis and Crandall	30 cc. water. Stirring 200 r. p. m.	O_2	25	0.0012	4.5 × 10^{-9}	3.7 × 10^{-6}
2	Davis and Crandall	30 cc. *sym.*-tetrachloro-ethane 200 r. p. m.	O_2	25	.006	50 × 10^{-9}	8.3 × 10^{-6}
3	Davis and Crandall	100 cc. water. Stirring 400 r. p. m.	O_2	25	.0012	2.6 × 10^{-9}	2.2 × 10^{-6}
4	Davis and Crandall	100 cc. 1 N K_2SO_4 + $Fe(OH)_2$. Stirring 400 r. p. m.	O_2	25	.0008	1.0 × 10^{-9}	1.3 × 10^{-6}
5	Davis and Crandall	100 cc. water. Stirring 400 r. p. m.	CO_2	25	.032	94 × 10^{-9}	2.9 × 10^{-6}
6	Becker	100 cc. water containing $FeSO_4$ and KOH. Stirring 1000 r. p. m.	O_2 +			5.2 × 10^{-9}	
7	Becker	590 r. p. m.				4.2 × 10^{-9}	
8	Becker	340 r. p. m.				2.9 × 10^{-9}	
9	Becker	140 r. p. m.				1.6 × 10^{-9}	
10	Becker	80 r. p. m.				1.3 × 10^{-9}	
11	Becker	60 r. p. m.				0.8 × 10^{-9}	
12	Becker	0 r. p. m.				0.03 × 10^{-9}	
		II. Gas Bubbled in Liquids					
13	Adeney and Becker	Tip of 15 cc. bubbles	Air	25	0.00079	50 × 10^{-9}	63 × 10^{-6}
14	Adeney and Becker	Sides of 15 cc. bubbles	Air	25	.00079	7 × 10^{-9}	8.9 × 10^{-6}
15	Adeney and Becker	Sides of 15 cc. bubbles	O_2	35.1	.00093	10.6 × 10^{-9}	11.4 × 10^{-6}
16	Adeney and Becker	Sides of 15 cc. bubbles	O_2	25.2	.0011	11 × 10^{-9}	10 × 10^{-6}
17	Adeney and Becker	Sides of 15 cc. bubbles	O_2	15.5	.0013	11 × 10^{-9}	8.5 × 10^{-6}
18	Adeney and Becker	Sides of 15 cc. bubbles	O_2	2.5	.0018	11.3 × 10^{-9}	6.2 × 10^{-6}
19	Ledig and Weaver	Small bubbles	CO_2	25	.033	680 × 10^{-9}	20 × 10^{-6}
		III. Shaken Liquids (400 times per min.)					
20	Conant and Scherp	15 cc. water	O_2	25	0.0012	28 × 10^{-9}	23 × 10^{-6}
21	Conant and Scherp	15 cc. water satd. with oleic acid	O_2	25	.0012	24 × 10^{-9}	20 × 10^{-6}
22	Conant and Scherp	15 cc. water	H_2	25	.0007	25 × 10^{-9}	36 × 10^{-6}
23	Conant and Scherp	15 cc. water satd. with oleic acid	H_2	25	.0007	19 × 10^{-9}	27 × 10^{-6}
24	Conant and Scherp	5 cc. tetrachloro-ethane	O_2	25	.0076	160 × 10^{-9}	21 × 10^{-6}
25	Conant and Scherp	5 cc. tetrachloro-ethane	H_2	25	.0031	86 × 10^{-9}	28 × 10^{-6}
26	Conant and Scherp	5 cc. bromobenzene	O_2	25	.008	210 × 10^{-9}	26 × 10^{-6}

+ Calculated from the results obtained with air.

rates of absorption of oxygen and nitrogen at practically constant pressure from bubbles (vol., 15 cc.) moving upward through 94 cc. of water in a cylindrical tube 1 cm. in diameter; velocity of bubble upward, 10 cm. per sec.; velocity of water past cylindrical part of bubble through an annular space 0.05 cm. thick, 65 cm. per sec.

IIB.—Ledig and Weaver[15] measured the rate of carbon dioxide absorption at atmospheric pressure from bubbles, vol. 0.036 cc., suspended in downflowing water.

III. Liquids in a Shaken Absorption Chamber.—Conant and Scherp[16] have measured the rates of absorption of gases by 5–15 cc. of liquids when shaken in a 70-cc. flask 400 times a minute. Direct measurements showed the area of the liquid and wetted glass surfaces exposed during the shakings to be 50–75 sq. cm. A closer estimate was then made by determining the ratio of the over-all rate of ethylene absorption by concentrated sulfuric acid during shaking, to that at rest. This ratio was 5.6 and the area of the liquid surface at rest 11.5 sq. cm. On the assumption that the over-all rate of this particular absorption is proportional to the area of the acid surface and unaffected by the degree of its agitation,[4] the area during shaking was calculated to be 64 sq. cm.

Measurements carried out with the dissolved gases in the liquids at different degrees of saturation showed that the absorption rates satisfy fairly well the equation of Lewis and Whitman

$$\frac{dN}{A\,dt} = k_L(C_i - C_l)$$

Discussion

The Speed of Stirring and the Absorption Rate.—Becker measured the rates of oxygen absorption per unit area from air by suspensions of ferrous hydroxide stirred at various speeds (Expts. 6–12). He found the rate to be constant at any one speed, a result which has been confirmed by the writers, and he assumed it to be the same as the initial absorption rate by pure water (compare Expts. 3 and 8).

It will be seen that in Becker's experiments the absorption rate increased enormously with the stirring at first but tended to a maximum independent of further increases in the stirring speed. The value at 1000 r. p. m. was 5.2×10^{-9} mole per sq. cm. per sec., which is undoubtedly lower than the initial rate for pure water as pointed out below. (Unfortunately Becker did not record the quantities of ferrous sulfate and potassium hydroxide used.) Now Adeney and Becker (Expt. 16) found the value 11×10^{-9} mole per sq. cm. per sec. for the absorption rate of oxygen from the sides of bubbles. Considering the fact that in their experiments

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[15] Ledig and Weaver, THIS JOURNAL, 46, 650 (1924).

[16] Conant and Scherp, unpublished data from the Converse Chemical Laboratory, Harvard University.

the water was streaming past the sides through an annular space **0.05** cm. thick at the rate of 65 cm. per sec. it appears that this value represents about the maximum oxygen absorption rate that could be obtained into pure water stirred without breaking or enlarging the surface.

If currents brought fresh liquid continually to the very surface, the absorption rate per unit area should increase almost proportionally with the degree of agitation nor would it tend to a maximum. Thoughtful consideration of these facts impresses one with the reality of the liquid stationary film.

The Effect of Renewing the Surface.—Adeney and Becker found oxygen to be absorbed at a faster rate (about 7.5 times) from the tip of bubbles than from the cylindrical portion and they offered the following explanation. "The rate at which the water streams past the head of the bubble is much less than that at which it passes down the cylindrical portion of it; hence the absorption due to the head of the bubble is much greater than might be expected from its area." But this would mean that agitation below the liquid surface decreases the rate of oxygen absorption whereas Becker has shown that exactly the reverse is true. The writers suggest that the greater absorbing power of thk head of a bubble is caused by a continual pulling out laterally of the surface in front, which brings fresh water into the stationary film. On the other hand, the surface slides down the cylindrical portion without changing in area. The fact that the average absorption rate per unit area was found to be the same from this portion in bubbles of different sizes proves that a uniform oxygen gradient was very rapidly established through the film, in agreement with the calculations in the last section.

Ledig and Weaver's value for the absorption rate of carbon dioxide by water represents the average for the whole surface of small bubbles and their value for $k_L \times 10^6 = 20$ (Expt. **19)** lies between those of Adeney and Becker for the head and for the sides of large bubbles.

The film coefficients calculated from Conant and Scherp's experiments (20-26) $k_L \times 10^6 = 20\text{–}36$ are almost half that for the head of bubbles in water. It appears that if the volume of the containing vessel is much greater than that of the liquid, then tossing it back and forth, continually spreads out new liquid surfaces on the walls and is an excellent way to secure high absorption rates. Under these conditions, diffusion no longer plays the dominating role in limiting the absorption. Currents in **the film** have become an important factor also.

A Comparison of the Rates of Solution of Gases by Water and by Organic Solvents.—In the experiments with stirred liquids the film diffusion coefficient k_L of tetrachloro-ethane was over twice that for water under the same conditions. On the other hand, in Conant and Scherp's experiments with shaken liquids, the coefficients were practically the same for absorption of oxygen and hydrogen into water, tetrachloroethane and bromobenzene. The magnitude of the absorption rate depended almost entirely on the solubility of the gas.

Hydrogen **and** Oxygen.—The film coefficients for hydrogen in Conant and Scherp's experiments are 1.3 to 1.4 times those for oxygen under the same conditions; but data in "International Critical Tables" show that hydrogen diffuses about 2.4 times faster than oxygen in liquids. Perhaps this bears out the assumption of Lewis and Whitman that the liquid film diffusion coefficients for all solutes are of about the same magnitude.

Absorption Rate and Reaction Rate.—When a gas, oxygen for example, is absorbed by a solution and reacts irreversibly with some substance dissolved therein, steady conditions are often reached where the rate of oxygen absorption is just equal to the rate at which it is consumed in the solution. What is the concentration of the dissolved oxygen? Evidently not the saturation value, for oxygen could not then be absorbed at all. If the absorption rate at the steady state is less than the initial physical absorption rate into the pure solvent, then an estimate of its fractional saturation in the solution will be obtained from the ratio of these rates. Hence the importance of determining the initial absorption rate.

Suspensions of ferrous hydroxide in dilute solutions can be used conveniently for finding the order of the value for the initial rate of oxygen absorption by water in an apparatus. However, experiments 3 and 4, Table II, show that the rate for a suspension in 1 N potassium sulfate is less than half that for pure water and the fact that the film diffusion coefficient is also lower shows that the effect is not entirely due to the lowering of the oxygen solubility by the potassium sulfate.

Miyamoto[17] has shown that when air is bubbled through suspensions of ferrous hydroxide in sodium hydroxide solution, the over-all absorption rate is independent of the quantity of the precipitate but is reduced by the addition of more alkali. It is to be regretted that absorption rates per unit area of surface cannot be calculated from the extensive data of this investigator.

If the oxygen absorption rate is greater than the initial rate it means that the main body of the solution contains little or no dissolved oxygen and that part or all of the reaction takes place in the liquid stationary film. This will be treated further in another communication.

Summary

1. The reality of the liquid stationary film, the thin unstirred layer, on the surface of liquids is emphasized. The important role of this film in gas absorptions, though known to engineers, has not perhaps been generally recognized. Its effective thickness depends on the absorption conditions.

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[17] Miyamoto, Bull. *Chem. Soc., Japan,* *2,* *40* **(1927); 3, 137 (1928); 4,** *65* **(1929);** *Sci. Papers Inst Phys. Chem. Research* (Tokyo), *7, 35* **(1927); 9, 203 (1928).**

2. When a pure gas is suddenly brought into contact with a liquid, a gradient of dissolved gas, tending to uniformity, is rapidly built up through the film. The rates at which the gradients are established in oxygen absorption by water have been calculated for different effective thicknesses of the stationary film corresponding to various conditions of liquid agitation. In well-stirred water the gradient becomes practically uniform in a fraction of a second.

3. The absorption rate after stationary gradient conditions have been established in the film (initial absorption rate) is the maximum at which dissolved gas can reach the main body of the solution. At any time, for a moderately soluble gas, the rate is proportional to the fractional unsaturation of the liquid with dissolved gas.

4. The initial absorption rates per unit area of surface and the liquid film diffusion coefficients have been calculated from data on gas absorptions by water and a few organic liquids for (a) stirred liquids, (b) gas bubbles and (c) shaken liquids.

5. The absorption rate for liquids stirred without breaking the surface increases with the stirring but tends to a maximum. For oxygen absorption by water, this maximum appears to be about the same as the rate from the sides of cylindrical bubbles moving rapidly through deoxygenated water, 11×10^{-9} mole per sq. cm. per sec. at 25°.

6. Adeney and Becker showed that air is absorbed faster, per unit area of surface, from the head of a cylindrical bubble than from the sides. It is suggested that this phenomenon is caused by film renewal at the head where the surface is continually pulled out laterally. The absorption rate per unit area for shaken liquids can become greater than the maximum with stirring, due apparently to the continual spreading out of the surface layer.

7. With stirring, the liquid film diffusion coefficients of water were less than, but of the same order as, those of organic liquids under the same conditions. With shaking the coefficients were practically identical for all the liquids. The absorption rates were then simply proportional to the solubilities of the gases.

8. It is suggested that the ratio of absorption rate of a pure moderately soluble gas by a liquid under any one set of conditions, to the initial absorption rate under the same conditions, affords a measure of the fractional unsaturation of the liquid with gas. If the gas reacts with the solvent itself, an inert gas of similar solubility could be used.

9. Where the effects of foreign substances on rates of reaction in solution are being measured by the rates of absorption or evolution of gases, the importance of also checking up their effects on the initial absorption rate of the gas is suggested.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY. MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 64]

THE ROLE OF THE LIQUID STATIONARY FILM IN BATCH ABSORPTIONS OF GASES. II. ABSORPTIONS INVOLVING IRREVERSIBLE CHEMICAL REACTIONS[1]

BY HAROLD S. DAVIS[2] AND GEORGE S. CRANDALL[3]

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In the preceeding communication[4] it was pointed out that under fixed absorption conditions (agitation, temperature, gas pressure, etc.), the *initial* absorption rate is the highest at which a gas can pass by physical dissolution into the main body of a liquid.

The present paper deals with the relationships between the absorption rate and other factors when the gas reacts irreversibly in the solution. With rapid reactions the rate of absorption can be much greater than the initial speed of pure physical solution.

Let us consider the absorption of a pure gas through an unbroken surface into a well-stirred liquid, when any irreversible chemical reactions taking place are instantaneous compared to the rate of absorption. The following postulates will be made for these conditions.

1. The effect of the gas film is negligible and the surface of the liquid is kept saturated with gas.
2. The main body of the liquid is homogeneous right up to a sharply defined surface that marks the inner limit of the stationary liquid film.
3. The specific diffusivity of each solute through the liquid stationary film is the same.[5]

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[1] This paper contains results obtained in an investigation on the "Relative Rates of Reaction of the Olefins," listed as Project No. 19 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 coöperation of the Central Petroleum Committee of the National Research Council.

[2] Director and Research Associate, Project No. 19.

[3] Junior Research Fellow, Project No. 19.

[4] Davis and Crandall, THIS JOURNAL, 52, 3757 (1930).

[5] This is the assumption originally made by Lewis and Whitman, *Ind. Eng. Chem.*, 16, 1215 (1924), and there is indeed a surprising similarity in the values which have been found for the coefficients of diffusion of solutes in aqueous solution under similar conditions (see "International Critical Tables," Vol. V, pp. 63–72). On the other hand, Schwab and Beringer, *Z. physik. Chem.*, 138A, 55–74 (1928), concluded that the liquid film diffusion coefficients for five permanent gases in water were practically the same at 20° but changed relatively to each other as the temperature was raised. The results of these investigations are somewhat puzzling. Although they claim an accuracy of 10% for their experiments (bubble method of Adeney and Becker, *Phil. Mag.*, 39, 385 (1920)), yet values for the solubilities of the gases calculated from their data show large deviations from those obtained by other investigators, as the table shows.

The concentration gradients which will now be examined are those existing in the film after a uniform absorption (initial absorption rate) has been reached but while the concentration of the reaction products in the main body of the liquid is still negligible.

Case **A.** The Absorption of a Pure Gas by a Liquid **with** which it Does not React Irreversibly.—This case has been considered in our previous communication; however, for the purpose of comparison, the conditions in the film are shown diagrammatically in Fig. 1, Case A. The sloping line denotes the gradient of decreasing concentration of the dissolved gas inward from the surface. It is uniform because the same quantity of solute passes per second through each unit cross section of the film made parallel to the surface.

$(\mathrm{d}N)/(A\,\mathrm{d}t)$Init. $= k_\mathrm{L}C_\mathrm{i}$ or in general as the gas builds up in the main body of the solution $\mathrm{d}N/A\mathrm{d}t = k_\mathrm{L}(C_\mathrm{i} - C_\mathrm{L})$. The same nomenclature is used as in the preceding article.

Case B. The Absorption of a Pure Gas by a Solution of a Substance with **which** it Reacts Irreversibly in One Stage and Mole **for Mole.**—The position of the Zone **A,** Fig. 1, Case B, at which the reaction takes place will depend on the relative magnitudes of C_i and C_S, the concentrations of the gas at the interface and of the solute in the main body of the solution, respectively.[6]

COMPARISON OF DATA ON SOLUBILITIES OF GASES IN WATER

a = cc. gas (at 760 mm. and 0°) dissolved by 1 cc. liquid when partial pressure of gas is 760 mm.

	O_2				H_2	
	20°	30°	60°	80°	20°	30°
Schwab and Beringer	0.020	0.021	0.016	0.016	0.018	0.016
Landolt–Bornstein–Roth "Tabellen"	0.031	0.026	0.019	0.017	0.018	0.017
Adeney and Becker	0.029	0.025	...	...	...	...

	CO_2			C_2H_4		C_2H_2	
	20°	30°	60°	20°	30°	20°	30°
Schwab and Beringer	0.68	0.50	0.34	0.10	0.08	0.67	0.63
Landolt–Bornstein–Roth "Tabellen"	0.88	0.67	0.36	0.12	0.10	1.0	0.84
Adeney and Becker	..	..	..	..	..	..	..

Further, it would appear from their data that the initial absorption rate of oxygen by water at 30° is almost twice that at 20°, whereas Adeney and Becker found it less. Until these discrepancies have been explained, some hesitation must be felt in accepting the conclusions of Schwab and Beringer that the differences in the diffusivities, calculated from their data, indicate the degrees of hydration of the dissolved gases.

[6] Similar diagrams of the concentration gradients of the reactants and of the reaction zone for the dissolution of a solid in a solution of a substance with which it reacts have been given by Brunner [Z. *physik. Chem.*, *47*, **67**, *et seq.* (1904)]. The similarity of the liquid stationary film at the two types of interfaces should be emphasized. Weber and Nillson, *Ind. Eng. Chem.*, 18, **1070 (1926).** and Hatta, *Tech. Reports Tohôku Imp. Univ.*, 8, 1 (1928), have also given diagrams of concentration gradients in films.

The quantities of dissolved gas and solute diffusing to the reaction zone in unit time and of the reaction product diffusing away are equal and it is evident that

$$\frac{(\mathrm{d}N)}{(A\,\mathrm{d}t)\mathrm{Init.}} = k_L(C_i + C_S)$$

The molar concentration of the reaction product between the surface and the reaction zone is uniform and equivalent to that of the solute in the main body of the solution. If the solubility of the reaction product is low and its metastable limits are exceeded, it may precipitate as a solid or liquid (the case of a gas is not considered here) which tends to fall into the main body of the liquid or rise to the surface. In any case the presence of the precipitated reaction product will cut down the absorption and may almost stop it.

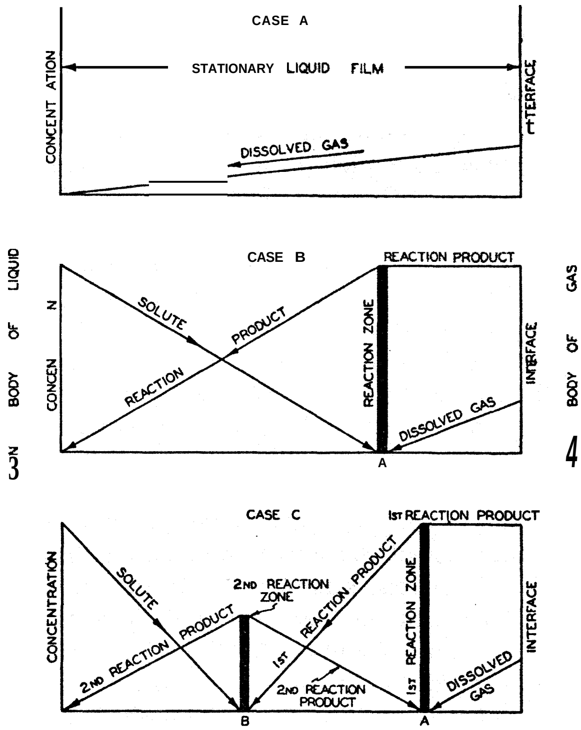

Fig. 1

Case C. The Absorption of a Pure Gas by a Solution of a Substance with which it Reacts in Two Stages in Instantaneous Irreversible Reactions (Fig. 1, Case C).—As in Case B the primary reaction product exists in uniform concentration between the first reaction zone and the surface. The secondary reaction product diffuses in both directions from the second zone but never reaches the surface.

$$\frac{(\mathrm{d}N)}{(A\mathrm{d}t)\text{Init.}} = k_L(C_i + C_S)$$

The following factors have not been considered in these pictures: (1) the time required for the completion of the reactions (they are assumed to be instantaneous with respect to the diffusion rates); (2) the effects of the reaction products on the solubility of the gas; (3) the effects of the reaction products on the effective thickness of the stationary film and on the diffusivities of the solutes; (4) the heat produced in the film by the reactions. (It must also flow away by diffusion since it is assumed convection plays a minor part in the film.)

Keeping in mind these limitations, which will be considered later, the main conclusions from these pictures will now be tested by experimental data of the authors and other investigators.

Experimental Part.—The apparatus used was that described in the preceding paper in which gas absorptions can be carried out at constant volume or at constant pressures into a known area of liquid surface while the liquid is being stirred beneath the surface.

General Relationship.—According to these postulates the rate of absorption of a pure moderately soluble gas by a concentrated solution should be largely independent of the gas pressures (since C_i is negligible compared to C_S) and the experiments at constant volume showed this to be indeed the case. Even in the absorption of sulfur dioxide by 1.8 M potassium hydroxide, Expt. 13, Table I, the pressures decreased almost uniformly with time, about four-fifths as much gas being absorbed per second at one-fifth as at one atmosphere. It may be seen from Table I that under similar conditions there is a qualitative agreement between the ratios of the rates of absorption determined experimentally (Col. 9) and the ratios calculated on the simple assumption that the rate is proportional to $(C + C_S)$ (Col. 10). The relationship appears to be valid in the absorption of carbon dioxide by water and by very dilute alkaline solutions (Expts. 2, 4, 5) but falls down as the concentration of the solute is increased (Expts. 6, 7, 8 and Table II). Even when the gaseous solubilities are quite different, the relationship still holds, *e. g.*, Expts. 12, 13, and a remarkable agreement is found in the absorption of ethylene by bromine water (Expt. 11), even though the reaction is quite different. Detailed treatment of the absorption of ammonia by water and by hydrochloric acid is given later. Nevertheless, the relationship is only qualitative and a more exact one must include the four neglected factors noted above. For this purpose the following studies of the absorption of carbon dioxide by water and by alkaline solutions are presented.

TABLE I
EXPERIMENTAL DATA

No.	Gas	Liquid	R. p. m.	C_i	C_S	$\frac{(dN)}{(A\,dt)}$ Init. $\times 10^9$	$k_L \times 10^6$ (exptl.)	Ratios of absorption rates Exptl.	Calcd. assuming k_L = const.	Calcd. corrected for change of k_L
			Authors' experiments							
1	O_2	100 cc. water	400	0.0012	..	2.57	2.15	0.028	0.036	..
2	CO_2	100 cc. water	400	.033	..	94	2.85	1	(1)	(1)
3	CO_2	100 cc. 0.1 *M* $NaHCO_3$	400	.030	..	60	2.0	0.64	0.9	..
4	CO_2	100 cc. 0.1 *M* NaOH	400	.030	0.1	218	..	2.3	3.9	2.9
5	CO_2	100 cc. 0.1 *M* Na_2CO_3	400	.030	.1	235	..	2.5	3.9	2.9
6	CO_2	100 cc. 1.2 *M* Na_2CO_3	400	.03[a]	1.2	170	..	1.8	37	15
7	CO_2	100 cc. 2.3 *M* KOH	400	.03[a]	2.3	1850	..	19.7	71	21
8	CO_2	100 cc. 2.6 *M* NaOH	400	.03[a]	2.6	1300	..	13.8	80	22
9	CO_2	100 cc. 12 *M* KOH	400	...	12	1600	..	..	..	..
10	CO_2	100 cc. 12 *M* KOH	0	...	12	5100	..	..	..	..
11	C_2H_4	100 cc. 0.85 *M* Br_2 in 2 *M* KBr	400	.04[a]	0.85	1560	..	16.6	27	..
12	CO_2 (0.5 atm.)	100 cc. 1.7 *M* KOH	600	.016[a]	1.74	1800	..	1	(1)	..
13	SO_2 (0.5 atm.)	100 cc. 1.8 *M* KOH	600	.73[a]	1.80	4300	..	2.4	1.5	..
			Whitman and D. S. Davis experiments							
16	NH_3	Water	60	0.62	..	580	..	1	(1)	..
17	NH_3	2.3 *M* HCl	60	...	2.3	1100	..	2	3.7	..

[a] Approximate values.

TABLE II

LEDIG AND WEAVER'S DATA ON THE ABSORPTION OF CARBON DIOXIDE FROM BUBBLES

No.	Concn., *M*	Ratios of absorption rates Experimental NaOH	 KOH	 Calcd.
1	0	1.0	1.0	(1.0)
2	0.2	2.8		4.3
3	.5	5.6	7.5	8.8
4	1.0	9.0	11.0	13.7
	1.27	Saturation concn. of $NaHCO_3$		
5	1.5	10.5		16
6	2.0	11.0	16.0	20
7	2.5	11.5		21
	2.7	Saturation concn. of Na_2CO_3		
8	3.0		18.0	23
	3.25	Saturation concn. of $KHCO_3$		
9	3.3	11.0		
10	4.5		19.0	
	5.9	Saturation concn. of K_2CO_3		
12	6.0		19.0	
13	6.6	5.0		
14	7.0			
15	7.5		19.0	

TABLE III

ABSORPTION RATES OF THE OLEFINS INTO QUIESCENT AND INTO STIRRED SULFURIC ACID AT 25°

Expt.	Olefin	Concn. of H_2SO_4, %	R. p. m.	$\frac{(dN)}{(Adt)\text{Init.}} \times 10^9$	*Cof.* × 10^4	*Cof.* × 10^4 (Davis and Schuler)
		(A) Experiments at constant volume				
E 1	Ethylene	95.8	0	6.04	1.48"	1.4
			90	6.04	1.48	1.8 (28)[b]
			480	6.04	1.48	
			1000[c]	61.2	15	
E 2	Propene	80	0, 200, 250–360	12.5	3.07	3.99 (28)[b]
E 3	Isobutene	70	0	204	50.1	58.9
			120–240	317	77.5	57.8 (28)[b]
E 4	Isobutene	70	0	243	59.4	
			88	287	70.4	
E 5 (a)	Isobutene	60	0	66.3	16.25	14.7
(b)			120–240	53.9	13.20	9.7 (28)[b]
			0	63.9	15.65	
(c)			120-240	55.8	13.65	
			0	60.8	14.85	
		(B) Experiments at constant pressure				
E 6	Isobutene	60	0	53.2	15.5	14.7
			220	59.2	14.5	9.7 (28)[b]
E 9[d]	Isobutene	60	200	47.4	11.6 at 0%[e]	
			200	50.2	12.3 at 10%	
			200	65.5	13.6 at 20%	

TABLE III (*Concluded*)

Expt.	Olefin	Concn. of H_2SO_4, %	R. p. m.	$\frac{(dN)}{(A\,dt)\text{Init.}} \times 10^9$	Cof. × 10^4	Cof. × 10^4 (Davis and Schuler)
			200	57.8	14.1 at 30%	
			200	57.8	14.1 at 40%	
			200	420	10.3 at 50%	
E 10[d]	Propene	87	600	150	36.6 at 0%	36.2 (28)[b]
			600	122	29.8 at 10%	
			600	106	26 0 at 20%	
			600	92	22.5 at 30%	

[a] Mr. H. W. Scherp, working at the Harvard Chemical Laboratory, obtained the value Cof. = 1.8×10^{-4}, using the very same acid and ethylene that was used in our experiments. He used an apparatus with a sensitive manometer filled with tetrachloro-ethane (sp. gr. 1.6) and a compensator to avoid the necessity of correcting for changes in barometric pressure. [b] Revolutions per minute of rotating absorption chamber. [c] The surface of the liquid was drawn down in the center and thrown up on the sides by the rapid stirring so that its area was greatly increased. [d] These experiments were performed in the small chamber with 1 cc. of acid, [e] Quantity of isobutene absorbed. 100% = 1 mole isobutene per 1 mole sulfuric acid.

Hatta[7] has investigated the rates of absorption of carbon dioxide by stirred solutions of potassium hydroxide. He concluded that the reaction to bicarbonate is slow, being negligible in the film, while the reaction to normal carbonate is instantaneous at a zone inside the film. Accordingly the concentration gradients at the stationary state should be of the type shown in Case B of Fig. 1 (except that two moles of hydroxide unites with one of the dissolved gas).

However the writers submit for consideration the following evidence that the reaction to bicarbonate is rapid, taking place principally in the film, and that the concentration gradients are of the type shown in Case C of Fig. 1.

1. The initial rate of absorption of carbon dioxide by 0.1 M sodium carbonate is considerably higher than the initial rate of physical dissolution into pure water (Expts. 2 and 5, Table I). Indeed it is practically the same as that of 0.1 M sodium hydroxide. This was proved not only by experiments with prepared solutions of the two but also by following the absorption rate at constant pressure into 0.1 M sodium hydroxide until no more gas was absorbed. The rate at the stage represented by complete transformation to normal carbonate was almost exactly half the initial rate, and the total quantity absorbed corresponded to that necessary to form bicarbonate and physically to saturate the solution.

2. There is strong evidence that sodium bicarbonate precipitates in the stationary film when carbon dioxide is absorbed by solutions of sodium hydroxide or sodium carbonate stronger than approximately 1.5 *M*. When carbon dioxide is brought into contact with quiescent 2.5 *M* sodium

[7] Hatta, *Tech. Reports Tohôku Imp. Univ.*, 8, 1 (1928).

hydroxide, the whole surface is soon covered with a mat of crystals. These cannot be the normal carbonate because sodium hydroxide of this concentration will readily dissolve an equal molecular quantity of sodium carbonate and it is difficult to conceive how in a closed space the concentration of carbonate in the surface layer could ever exceed by very much, that of the hydroxide in the main body of the solution. Hence the crystals must be sodium bicarbonate. This conclusion is confirmed by the observation that crystals can be seen to form on the quiescent surface of sodium carbonate about three-quarters saturated, when allowed to stand in contact with carbon dioxide.

The phenomena stood out still more clearly under the microscope at about fifty diameters magnification. The solution to be examined was placed in a small cell 12 mm. wide and 2 mm. deep made by cementing a glass ring upon a slide. The cell and the objective of the microscope were surrounded by a glass cylinder 22 mm. wide and 25 mm. deep pressed tightly against the slide. The carbon dioxide was introduced through a side tube in the cylinder so that the whole solution was covered with the gas at substantially atmospheric pressure. To facilitate observations some particles from a lead pencil were rubbed into the solution. As soon as the gas entered, the particles below the surface of the solution became agitated by thermal currents while those at the surface remained practically stationary. Precipitation in the film showed as a cloud which sometimes gradually and sometimes quickly (after a lapse of a few minutes) obscured the field of vision. The results were as follows

Solution	Observations
0.5 M NaOH	No cloud
1.3 M NaOH	Gradual dimming of field
2.6 M NaOH	Distinct cloud suddenly appearing after one to three minutes
2 6 M KOH	Field actually brightened, no cloud. Thermal currents rapid until alkali was neutralized by carbon dioxide
9 M KOH	Thick cloud in a little over one minute

These results should be studied in relation to Tables I and II and leave no doubt but that actual precipitation of either primary or secondary reaction product occurs in the liquid stationary film at approximately the concentration of alkali at which it would be predicted from our postulates. Visual observations, especially with the aid of a microscope, can be of great service in studies of these reactions which take place in the film.

The Effects of the Reaction Products on the Liquid Film Diffusion Coefficient.—Experiments 2 and **3,** Table I, show that the absorption rate of carbon dioxide by 0.1 M sodium bicarbonate was 36% less than by pure water, although the solubility was only decreased 8%. This indicates that the liquid film diffusion coefficient of the 0.1 *M* salt solution is only 0.7 times that for pure water. Figure 2 shows the general relationship (determined by separate experiments similar to 2 and 3) between the values for k_L, relative to that for pure water, and the concentration of bicarbonate. It is important, however, to note that this is not simply a salt effect because k_L for 1 *M* potassium chloride was found to be practically identical with that for pure water.

Using the corrected value for the film coefficient, the ratio of the absorption rates of either 0.1 M sodium hydroxide or 0.1 M sodium carbonate to that of pure water should be $0.7\ (0.1 + 0.030)/(0.033) = 2.8$, whereas the values actually found were 2.5 and 2.3. In a similar way the values in Col. 11, Table I, and in Col. 5, Table II, have been calculated.

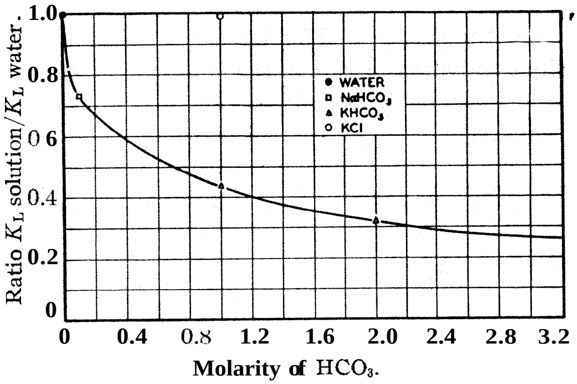

Fig. 2.

The legitimate objection will be raised that these modified values of k_L determined for bicarbonate solutions have been applied to the calculations in the absorption of carbon dioxide by solutions of caustic alkalies whereas bicarbonate exists only in the outer portion of the film. The writers can only suggest that the secondary product (normal carbonate) which exists in the inner portion may have a similar effect. At any rate, the agreements between the calculated and the experimental ratios is rather striking up to the point where the reaction product begins to precipitate. The effects of reaction products and of other substances on the liquid film diffusion coefficient offer a field worthy of further study.

Ledig and Weaver[8] measured the rates of absorption, per unit area, of carbon dioxide from bubbles into water, and into solutions of sodium and potassium hydroxides. By an ingenious device the bubble (vol. 0.036 cc.) was held stationary in the solution in a closed system by running the liquid downward at a rate sufficient to compensate for the tendency of the bubble to rise. The changes in volume were followed by the movement of the surface of the liquid in a capillary tube open to the atmosphere.

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[8] *Ledig and* Weaver, THIS JOURNAL, 46, 650 (1924); *Ledig, Ind. Eng. Chem.*, 16, 1251 (1924).

They state that "the rate is not constant during the whole period of absorption from a bubble (at constant pressure) but follows a three-stage cycle. This can best be seen in the absorption curves for very dilute solutions (see Fig. 3 reproduced from their article) and the higher concentrations undoubtedly follow the same course though this is not entirely evident if a curve is studied by itself. The cycle is begun by a very high absorption rate at the newly formed liquid–gas interface but as absorption goes on it falls again very quickly to a rate where an equilibrium condition exists, the rate being controlled by the diffusion of the reagent to the surface and of the reaction product away from the surface. The third stage in the cycle begins when the diluting gas starts to retard diffusion of gas to the surface. This latter state is undoubtedly affected by the diminished buoyancy or rate of rising as the bubble becomes smaller and there is a decrease in the stirring action which renews the absorbing liquid at the surface."

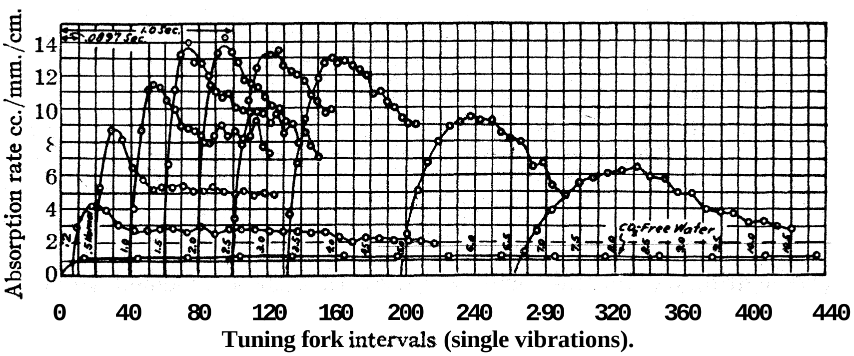

Fig. %.—Effect of concentration upon rate of absorption in NaOH solutions. (After Ledig and Weaver.)

Examination of the curves shows that no initial high absorption rate was detected in the case of absorption into pure water. This suggests that the high initial values clearly shown for absorption into sodium hydroxide solutions are caused by the hydroxide already in the freshly formed film. This diffuses outward to meet the carbon dioxide diffusing inward and the extension of the gradient of the latter into the film will increase, that is, the rate of gas absorption will decrease until the sodium hydroxide is diffusing uniformly from the main body of the solution into the film. The greater the initial concentration of the hydroxide in the film, the longer the time required to reach the conditions for constant absorption which might finally not appear at all. And this is exactly what the absorption curves show.

The initial absorption rate, by pure water, of carbon dioxide from the bubbles of Ledig and Weaver was $dn/(Adt)_{\text{Init.}} = 680 \times 10^{-9}$. This is over seventy times the value found by the writers (Table I) for water stirred underneath at 400 r. p. m. Nevertheless, the ratios of the rates into caustic solutions to that into pure water are very much the same in both cases. See, for example, 2.3 potassium hydroxide 19.1, Table I, and 3.0 potassium hydroxide 18, Table II. Apparently our generalizations hold for widely different absorption conditions.

Columns 3 and 4, Table II, give the ratios of the absorption rates at the stationary state found by Ledig and Weaver. Column 5 gives the ratios calculated on the assumption that they are proportional to $k_L (C_i + C_S)$. The results are striking. The calculated ratios for sodium hydroxide agree fairly well with the experimental up to the concentration where bicarbonate would be expected to precipitate, the experimental rates then remain constant up to a concentration somewhat beyond that of saturated sodium carbonate and finally steadily decrease. For potassium hydroxide the experimental and calculated ratios agree even better up to a point where potassium bicarbonate should precipitate, after which the former remain fairly constant for the range given in the table.

Ledig and Weaver found, however, no decrease in the rate for potassium hydroxide beyond a concentration corresponding to saturation of normal carbonate but on the contrary a rapid rise for concentrations somewhere above 9 *M*. They state "an attempt has been made to link this rapid rise of rate with the known properties of the solutions—solubility of the carbonates, viscosity of the solution and ionization of the hydroxide and carbonate solutions—but no quantitative relation has yet been found." The writers suggest that this phenomenon is caused by the large quantity of hydroxide brought into the film in the case of concentrated potash, by its renewal at the head[9] of the bubble. It has been pointed out that the period of persistence of the high preliminary rate increased with the concentration of the hydroxide. The quantity initially in the film for 0.1 M hydroxide was calculated to be about 1×10^{-7} mole. This is negligible compared to the amount of gas in the bubble, 1.3×10^{-5} mole, but the quantity for 6 M hydroxide, 0.6×10^{-5} mole, must play an important part in the absorption when the film is being renewed at the head. The conclusion is confirmed by the fact that in our experiments where the liquid was stirred without renewing the film, 12 M potassium hydroxide actually absorbed at a slower rate than 2.3 M solution.

Temperature Changes in the Film.—Adeney and Becker[10] found that the rate of oxygen absorption by water decreased slightly over the range 2.5 to 35.1°. The film coefficient increased almost 100% but was compensated for by a corresponding decrease in gaseous solubility.

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[9] For a discussion of the renewal at the head see Davis and Crandall, Ref. 4.

[10] Adeney and Becker, Phil. *Mag.*, 39, 391–402 (1920).

Nevertheless, these same investigators[11] have shown that oxygen is absorbed by water considerably faster from dry air than from air saturated with water vapor and have attributed this in part to local cooling of the surface layer by evaporation into the dry air. This indicates that considerable local temperature changes in the film may take place even for simple physical absorption of gases.

All the heat produced in the film by chemical reactions must flow away by diffusion to the surface or to the inner boundary, if convection plays only a minor part, so that the temperatures in the film will always be higher than in the main body of the solution. The writers found the rate of carbon dioxide absorption by unstirred 12 M potassium hydroxide to be three times that into the solution stirred at 400 r. p. m. Evidently a great rise in temperature takes place in the film of the liquid at rest and the absorption rate is high because of the increased solubilities of the reaction products and the increased film diffusion coefficient. Stirring helps to dissipate the heat into the main body of the liquid.

The Relative Rates of Carbon Dioxide Absorption by Solutions of Sodium Hydroxide and of Potassium Hydroxide.—The assumption of equal diffusivities for all solutes in the film appears to be only an approximation. Ledig and Weaver state that "potassium hydroxide solutions absorb carbon dioxide more than twice as fast as sodium hydroxide solutions at the lower concentrations." However, they compared the averages of the rates over the whole period of the absorption, including the high initial speeds. The ratio of the rates at the steady state (when uniform concentration gradients had been established) was about 1.5. This accords with the fact that the specific diffusivity of potassium hydroxide in dilute solutions is about 1.5 times that of sodium hydroxide. It seems clear that the differences in the absorption rates of carbon dioxide by the two is related to diffusivities and not to actual differences in the reaction rates as assumed by Hatta.[12]

The Experiments of Whitman and D. S. Davis.[13]—These investigators determined the rates of absorption where a gas was passed over 4 liters of liquid with 405 sq. cm. of surface exposed. Both gas and liquid were stirred by separate blades at 60 r. p. m. The following table has been prepared from their data.

Oxygen was absorbed so slowly that the over-all liquid film diffusion coefficient for this case was assumed to be identical with the true liquid film diffusion coefficient. However, in the fast ammonia absorption the surface could not become saturated because of the resistance of the gas film through which a considerable gradient had to be established in order:

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[11] Adeney and Becker, *Phil. Mag.*, 42, 92–93 (1921).

[12] *Hatta, C. A.*, 24, 763 (1930).

[13] Whitman and D. S. Davis, *Ind. Eng. Chem.*, *16*, 1233 (1924).

TABLE IV

DATA OF WHITMAN AND DAVIS

Solute	Average partial pressure of solute in air mixture, mm.	Liquid	$\left(\frac{dn}{Adt}\right)_{\text{Init.}}$	K_L (Over-all)
Oxygen	746	Water	$0\ 87 \times 10^{-9}$	0.92×10^{-6}
Ammonia	2.3	Water	580×10^{-9}	0.29×10^{-6}
Ammonia	19.09	2.3 *N* HCl	1100×10^{-9}	....

to convey the ammonia to the liquid surface at such a rapid rate. It will be assumed here that the fractional saturation of the surface layer is shown by the ratio of the over-all coefficient to the true coefficient $0.29/0.92 = 0.31$ (which is true if the gas follows Henry's law). Water at 30° saturated with ammonia at 21.3 mm. is about 2 *M*,[14] so that the surface concentration for the absorptions into water was 0.62 *M*.[15] Whitman and Davis assumed that during the absorption into 2.3 N hydrochloric acid the concentration of the ammonia in the surface layer was negligible. These values were used in calculating the ratios given in Table III (1 to 2.0 experimental and 1 to 3.7 calculated, the divergence may be due to changes in k_L).

Absorptions of Gaseous Olefins by Sulfuric Acid.—In a former communication[16] it was pointed out that the values of the absorption coefficient in a rotating chamber were characteristic for the separate olefins. It will be noted that values obtained in the new apparatus agree very well with the former ones (see Cols. 6 and 7, Table III). The absorption rates are expressed both as *Cof.* and as dN/AdT to facilitate comparisons of the latter values with the former. This agreement holds even where the ratio of liquid surface to liquid volume is changed over a large range (from 12.2 rotating and 2.45 sq. cm./cc. at rest in the former to 0.57 sq. cm./cc. in the new apparatus). As has been shown in that communication, the absorption coefficient *Cof.* calculated from the constant volume experiments should equal the rate at which the olefin would be absorbed at constant pressure, the gas being measured at that pressure. It will be noted that the initial rates of absorption at constant pressure agree well with the values of *Cof.* calculated from the constant volume experiments.

In the experiments with ethylene and propene using concentrated sulfuric acid, the absorption rate per unit area was not affected by stirring.[17]

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[14] Haslam, Hershey and Keen, Ind. *Eng. Chem.*, **16**, 1224 (1924).

[15] Whether or not the gas film is controlling in the absorption of a very soluble gas such as ammonia in water can be conveniently tested by measurements of the absorption under similar conditions by a solution (*e. g.*, hydrochloric acid), with which the dissolved gas reacts instantaneously.[13]

[16] Davis and Schuler, THIS JOURNAL, 52, 721 (1930). *Cof.* instead of *C* is used in the present paper for The Coefficient, because here *C* denotes concentration.

[17] The statement of Damiens, *Compt. rend.*, 175, 585 (1922), that stirring at 200

However, in the absorption of isobutene into 70% acid the rate of absorption **was** greater into the stirred acid than into acid at rest but within the range investigated was independent of the rate of stirring. Further, the rate at rest was irregular, falling off quite rapidly toward the end. In this experiment a layer of polymer insoluble in the acid was found on top of the acid at the end. For isobutene and 60% acid the absorption rate was less when the acid was stirred but independent of the rate of stirring (within the range investigated). The absorption curves for this experiment (Fig. 4, Nos. **E5A** and E5B) merit careful study. That of 5A (r. p. m. = 0) starts at a faster rate than that of 5B (r. p. m. = 240). When the stirring conditions were reversed the two curves cross. Finally, at the end for the same stirring conditions (r. p. m. = 0) the curves are parallel. All the reaction products in this case were soluble

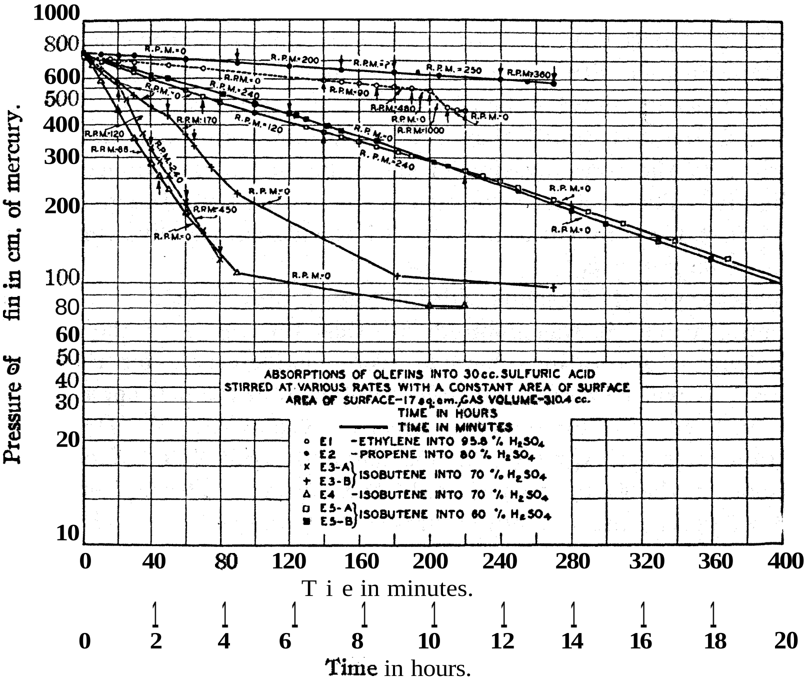

Fig. 4.

r. p. m. increases the absorption rate of ethylene by concentrated sulfuric acid **20–27** times has been frequently misinterpreted. Unfortunately the full experimental details are not given. He found the absorption rate to be proportional to the partial pressure of the gas and to the surface of contact.

The writers suggest that a method for determining the effective area of a liquid when stirred or shaken can be based on these facts. The over-all absorption rate of ethylene by concd. sulfuric acid under the same conditions of agitation should be divided by its absorption rate per unit area into the acid at rest.

in the acid. Further, *tert.*-butyl alcohol was salted out when the acid was neutralized in the cold with sodium hydroxide. The rate of absorption of isobutene at constant pressure by 60% acid increased as more olefin was absorbed up to 0.4 mole of isobutene per mole of acid and then fell off. However, in the absorption of propene by 87% acid the rate steadily decreased from the first.

It has been shown[16] that the physical solubilities of the olefinic gases in sulfuric acid are very low, and yet enormous rates of absorption are observed in some cases. It is inconceivable that under these conditions the dissolved olefin could penetrate to and react in the main body of the liquid. The entire reaction must take place either at the surface or in the stationary film. In the latter case it can only penetrate a short distance because the concentration gradients from the surface must be very steep. For instance, 500×10^{-4} cc. of propene was absorbed per sec. per sq. cm. by 97% sulfuric acid and a uniform gradient carrying oxygen under atmospheric pressure into water at that rate could only extend in from the surface about 0.00001 cm.

The conclusion that the olefin never reached the main body of the liquid in our experiments is confirmed by the facts that the absorption rates were in the majority of cases unaffected by stirring underneath the surface or by changing the acid volume.[18]

The conclusion that the reaction does take place inside the film rather than at the interface is confirmed by the experiments with isobutene. As pointed out above, the absorption rate of isobutene into an excess of 60% sulfuric acid at rest rises slightly as the absorption proceeds. The rate is brought back to normal if the solution is stirred. At constant pressure, with stirring, the rate per unit area increases slowly to a total absorption of 0.4 mole per mole of sulfuric acid and then slowly decreases. When isobutene is absorbed by acid of this concentration, *tert.*-butyl alcohol is formed directly[19] and is only slowly polymerized at 25°. The sulfuric acid functions as a catalyst for the union of water with the olefin. The intermediate sulfate has never been isolated. It seems reasonable to attribute the "abnormal" effects just cited to the *tert.*-butyl alcohol. This accumulates in the film of the unstirred liquid until its rate of diffusion into the main body of the acid equals the rate of formation. Its presence increases the solubility of the isobutene and hence the absorption rate is higher. This illustrates again how much the presence of reaction products may affect an absorption rate. It has actually given rise to a maximum in the rate of absorption in this case.

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[18] Plant and Sidgwick, *J. Soc. Chem. Ind.*, 40, 14–18T (1921), absorbed ethylene into concentrated sulfuric acid by bubbling the gas through the liquid. Their assumption that "the liquid phase must be regarded as saturated with ethylene" appears to be unjustified.

[19] Michael, *Am. Chem. J.*, 38, 267–279 (1912).

On the other hand, the absorption of propene at constant pressure into stirred 87% acid decreases continuously with the quantity taken In. Here isopropyl sulfate is formed, which decreases the concentration of the acid. The separate olefins are absorbed at widely different rates by the same concentration of acid. It is concluded that the reaction rates of the dissolved olefins are different. However, the absorption rates cannot be directly proportional to the reaction rates. For, consider the case of two olefins of equal solubility but with reaction rates in the ratio 1:2; evidently, at any time, there is more of the slower reacting one in the solution, so that the quantity which reacts in unit time, and therefore its absorption rate, is more than half that of the other. The slower reacting one has an unfair advantage.

Summary

1. The two-film theory of gas absorption proposed by Lewis and Whitman has been extended to cases where rapid chemical reactions take place in the solution.

2. The reactions between the dissolved gas and a solute, for the cases studied, appear to occur inside the liquid. If the reaction rates are very fast compared to the rates of diffusion through the liquid film, then the reactions take place at zones in this film parallel to the liquid surface.

3. Diagrams are given of the concentration gradients in the film at the initial state of uniform gas absorption for instantaneous reactions taking place in one stage and in two. The primary reaction product exists between the surface and the first reaction zone, in concentration equal to that of the solute in the main body of the solution. If the metastable limit of its solubility is exceeded, it will precipitate.

4. A general equation is proposed for calculating the rate of absorption of a pure gas by a liquid (physical solution, or when reacting instantaneously with a solute) from its solubility, the concentration of the solute and the liquid film diffusion coefficient. The validity of this relationship is supported by calculations from gas absorption rate data of the authors and of other investigators for gases of widely different solubilities and for reactions of very different types.

5. A study is given of the rates of absorption of carbon dioxide by water and by solutions of sodium and potassium hydroxides. Conditions are described under which the precipitation in the film of a reaction product, sodium bicarbonate, can be seen during the absorption. Explanations are offered for the various phenomena observed by Ledig and Weaver regarding the absorption of carbon dioxide from minute bubbles by alkalies.

6. A study has been made of the effects of the reaction products on the magnitude of the liquid film diffusion coefficient. Some observations are given on the effects of the heat produced by reactions in the film.

7. The absorption rates of several olefin gases by sulfuric acid both at rest and stirred beneath its surface have been measured. The values for the absorption coefficients agree well with those obtained in a previous investigation using a rotating absorbing chamber.

8. The reactions between the olefins and sulfuric acid take place mainly in the liquid stationary film itself. This is indicated (a) by the enormous rates of absorption obtained in some cases, although the physical solubilities of the gases in the acid appear to be very low and (b) by the fact that stirring the acid underneath the surface or changing its volume, in most cases, did not change the absorption rate. The reaction rates of the dissolved olefins are quite fast and are not proportional to the absorption rates as is often assumed.

9. The fact that isobutene is absorbed by 60% sulfuric acid faster when the acid is at rest than when it is stirred is attributed to a greater accumulation of the reaction product, *tert.*-butyl alcohol, in the liquid stationary film of the quiescent acid.

10. It is suggested that the over-all rate of absorption of ethylene by concentrated sulfuric acid (the rate per unit area being independent of the agitation) may be used to determine the area of the surface of a liquid when stirred or shaken in an apparatus.

CAMBRIDGE, MASSACHUSETTS

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STUDIES IN GASEOUS OXIDATIONS. I. THE HOMOGENEOUS UNCATALYZED REACTION BETWEEN OXYGEN AND ACETYLENE

BY GEORGE B. KISTIAKOWSKY AND SAM LENHER

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The problem of the oxidation of hydrocarbons has been of great scientific and technical interest for many years. The present work was undertaken to study in detail the features of a simple hydrocarbon oxidation in the hope that it would contribute to the general knowledge of the mechanism of gaseous oxidations. Acetylene was chosen because it reacts with oxygen at lower temperatures than other hydrocarbons; this made it possible to isolate intermediate reaction products.

A systematic study of the slow reaction of simple hydrocarbons was initiated by Bone[1] about thirty years ago. More recently Pease[2] and also

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[1] Bone and Townend, "Flame and Combustion in Gases," Longmans, Green and Co., London, 1927.

[2] Pease and Chesbro, *Proc. Nat. Acad. Sci.*, 14, 472 (1928).

Pope, Dykstra and Edgar[3] and Thompson and Hinshelwood[4] have described experiments dealing with the slow thermal oxidations of the hydrocarbons by oxygen. Pease in particular has demonstrated that these reactions can occur in the gas phase exclusively and are inhibited by glass surface—a characteristic of chain reactions.

Bone and Andrew[6] studied the combustion of acetylene in sealed bulbs between 200 and 350°. They concluded that an excess of oxygen over and above an equimolecular proportion always retards the oxidation, and postulated the presence of an unstable product $C_2H_2O_2$(HOC≡COH), which decomposed directly to carbon monoxide and formaldehyde. Recently Briner and Wunenburger,[7] in studying the reaction between acetylene and ozone at low temperatures, found the liquid products of reaction to be mainly glyoxal, CHO—CHO.

Experimental Results

The oxidation of acetylene was studied by the flow method at atmospheric pressure. Acetylene and oxygen at a regulated rate of flow passed through separate purifying trains and were mixed at the entering point of the reaction vessel. Both gases were taken from commercial cylinders. Oxygen was freed from water vapor by passing it through two wash-bottles filled with concentrated sulfuric acid. Acetylene (Prest-O-Lite) was passed through two spiral wash-bottles containing water to remove acetone vapor and was dried over calcium chloride. The pyrex cylindrical reaction vessel, 22 mm. in diameter, was heated in a large electric tube-furnace. Temperatures were read by means of a chromel–alumel thermocouple enclosed in a thin-walled glass tube placed in the center of the reaction vessel.

The gases, after passing through a trap cooled in solid carbon dioxide, were led through a spiral wash-bottle containing a standardized barium hydroxide solution to absorb carbon dioxide quantitatively, and were collected in a water gasometer. The gas was transferred to a 500-cc. Hempel pipet containing alkaline pyrogallol solution and shaken until all oxygen was consumed; it was then transferred to a bromine water pipet, and acetylene was removed by shaking; bromine vapor was removed from the residual gas by shaking with potassium iodide solution in a small Hempel pipet. The gas was then analyzed for carbon monoxide and hydrogen in a Burrel gas analysis apparatus[8] after checking for absence of oxygen and acetylene. Gases originally containing less than 1% of carbon monoxide could be analyzed satisfactorily. Carbon dioxide was determined by titrating the barium hydroxide solution with hydrochloric acid. The condensable reaction products were determined by oxidation with standardized potassium dichromate solution in concentrated sulfuric acid and iodimetric titration of the excess potassium dichromate. The potassium dichromate solution was added from a buret to the trap while still cold so that even volatile products (formaldehyde) were included in the analysis. The condensable products were mainly formic acid and

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[3] Pope, Dykstra and Edgar, THIS JOURNAL, 51,2203,2213 (1929).

[4] Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), **125A,** 277 (1929).

[5] Semenoff, *Z. Physik,* 46, 109 (1927).

[6] Bone and Andrew, *J. Chem. Soc.,* **87,** 1232 (1905).

[7] Briner and Wunenburger, *Helv. Chim. Acta,* 12, 786 (1929).

[8] Bureau of Mines Bulletin No. 197, 1926; Bureau of Mines Technical Paper, No. 320, 1925.

formaldehyde. Checks with standardized formic acid solution showed that two equivalents of iodine are consumed in the oxidation of formic acid by potassium dichromate, the reaction being

$$HCOOH + {}^1/_2O_2 = CO_2 + H_2O$$

Oxidation of formaldehyde requires very nearly four (3.6) equivalents of iodine, the principal reaction being

$$CH_2O + O_2 = CO_2 + H_2O$$

although the other reaction

$$CH_2O + {}^1/_2O_2 = CO + H_2O$$

takes place to some extent.

A standard gas mixture containing equal volumes of acetylene and oxygen was used. The rate of flow of each gas was 0.1 cc./second, corresponding to an average contact time of 200 seconds for a 78-cc. vessel at an average temperature of 290°. Three hundred and sixty cubic centimeters of acetylene–oxygen mixture was used. Table I presents the results of these experiments. The amounts of formic acid and formaldehyde given in the last column have been calculated on the assumption that no other condensable products were present, and that these two substances were present in the ratio 6:1. Justification for this assumption will be given below in the discussion of the condensable products. From Table I it will be seen that the main products of acetylene oxidation are carbon monoxide and the "condensable matter." Carbon dioxide is also formed in considerable quantities whereas hydrogen, although present, plays a much less important role.

TABLE I

EFFECT OF TEMPERATURE ON REACTION OF OXYGEN WITH ACETYLENE

Average time of contact, 200 seconds

Temp., °C.	Moles passed × 10^3 C_2H_2	O_2	Moles formed × 10^3 CO	CO_2	H_2	HCOOH + HCHO
253	8.9	8.9	0.109	0.069	0.009	0.07
255	8.9	8.9	.074	.005	.022	.14
256	8.9	8.9		.021		.18
256	8.9	8.9	.126	.032		.07
Av. 255	8.9	8.9	.105	.032	.015	.11
Percentage of total carbon passed			.49	.18		.63
277	8.9	8.9	.25	.090	.043	.23
277	8.9	8.9	.43	.096	.057	.25
277	8.9	8.9	.29	.069	.039	.30
277	8.9	8.9	.25	.080	.035	.29
Av. 277	8.9	8.9	.30	.084	.043	.26
Percentage of total carbon passed			1.71	.43		1.50
296	8.9	8.9	0.99	.33	.087	
296	8.9	8.9	1.30	.38	.130	0.99
297	8.9	8.9		.39		.91
298	8.9	8.9		.40		.67
Av. 297	8.9	8.9	1.14	.37	.108	.84
Percentage of total carbon passed			6.4	2.1		4.7
315	8.9	8.9	2.67	0.80	.18	1.59
315	8.9	8.9	2.86	.70	.26	1.10
316	8.9	8.9	2.90	.77	.26	1.62
318	8.9	8.9	3.17	.91	.33	1.70
Av. 316	8.9	8.9	2.90	.80	.26	1.50
Percentage of total carbon passed			16.3	4.5		8.4

The composition of the condensable products, which in the above experiments were measured only by the amount of potassium dichromate consumed, was determined with a sample obtained by carrying out the reaction for twelve hours at 310–315°. One and six-tenths grams of condensed products was collected in the cooled trap and diluted with two cc. of water.

The resulting solution was opaque, and a small quantity of a resinous substance collected at the surface on standing. Small samples were withdrawn from the solution and analyzed. The condensate gave a positive test for formic acid, using the mercuric oxide test.[9] Titration of two samples with barium hydroxide indicated 56.1 and 53.3% of formic acid. Oxalic acid was not present, for no precipitate of barium oxalate was formed. Formaldehyde was determined by two methods: the potassium cyanide reaction,[10] which yielded in three determinations 4.7, 4.7 (small samples) and 5.4% (large sample) by weight, and the iodimetric method,[10] which yielded in three determinations 9.2, 8.3 and 8.9% by weight. These determinations accounted for about 65% by weight of the condensate. The chemical nature of the remainder was established by titrating another sample with standard potassium dichromate solution. If it is assumed that formic acid and formaldehyde were present in the ratio 55:9, the oxidation analysis gave their total amount as 71.7% of the condensate. The remaining 28.3% was non-oxidizable and was undoubtedly water.

The discrepancy between 64% obtained by acid and aldehyde determinations and 72% calculated from oxidation analyses we suspected was fictitious, and was due to the assumption that formaldehyde was the only aldehyde present. Condensate was collected for thirty hours to obtain material to test this point. This was added to a solution of 5 g. of p-nitrophenylhydrazine in 50% acetic acid solution and allowed to stand for thirty-six hours. The brick red precipitate was filtered off, neutralized with warm 10% sodium carbonate solution, washed with hot distilled water and dried. The precipitate was extracted with hot benzene to dissolve the nitrophenylhydrazone of formaldehyde.[11] The residue was recrystallized from hot pyridine, yielding brick red needles melting over the range 250–270°. As the di-*p*-nitrophenylhydrazone of glyoxal is the only probable *p*-nitro or di-p-nitrophenylhydrazone having a higher melting point than that of the formaldehyde compound (185°), it seemed clear that we were dealing with the glyoxal derivative. The di-p-nitrophenylhydrazone of glyoxal was prepared from glyoxal sodium bisulfite compound and on recrystallization gave a melting point of 305°. When the pure di-p-nitrophenylhydrazone of glyoxal was mixed with the derivative from the condensate (m. p. 250–270°), the mixture did not melt at 278°, but decomposition took place. The di-*p*-nitrophenylhydrazone of glyoxal derived from the condensate gave the characteristic Bamberger test[12] of a deep blue color with alcoholic potassium hydroxide. The characteristic color of the derivative from the condensate, the high melting point as well as the mixed melting point, and finally the color test shows that glyoxal was present in appreciable quantities in the condensate.

To complete the analysis of the condensable products, the water-insoluble resinous substance (3.78 mg.) was subjected to microcombustion after it had been dried for twenty-four hours by exposure to the atmosphere. This yielded 52.71% carbon, 8.65% hydrogen and 1.77% ash, the rest being undoubtedly oxygen. Such a compo-

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[9] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1905, Vol. I, p. 83.

[10] Allen, "Commercial Organic Analysis," 5th ed., P. Blakiston's Son Co., Philadelphia, 1927, Vol. I, p. 329.

[11] Rosenthaler, "Der Nachweis organischer Verbindungen," Verlag Ferdinand Enke, Stuttgart, 1923, 2d ed., p. 125.

[12] Bamberger, *Ber.*, 32, 1806 (1899).

sition does not correspond to any single substance probable under the circumstances and it must be assumed that a mixture was present. If one attributes all of the oxygen to water present in the analyzed sample (41.5% by weight), the composition is 1.0 carbon : 0.92 hydrogen, approximating the composition of acetylene. The behavior of the sample is further support for this assumption of water in the resinous matter, for it appeared to dry or harden on standing.

The effect of the time of contact on the speed of reaction and its course was studied by increasing the rate of flow. Results of these measurements made at two temperatures are presented in Tables II and III. In the experiments given in Table III, the condensate was weighed and the acid content determined by titration with barium hydroxide. The results of this determination are given in the last column together with the percentage weight of formic acid in the condensate. The experiments summarized in Table II show that the yields of all products decrease with the time of contact. This phenomenon finds an adequate explanation only in the assumption that the reaction exhibits an induction period. A more detailed consideration of Table II shows that the yields of various reaction products are not affected in the same way. The amount of carbon dioxide decreases most rapidly, then the carbon monoxide, while hydrogen and particularly the condensable substances diminish only very slightly in quantity. There appear to be two explanations of this specific influence of

TABLE II

EFFECT OF TIME OF CONTACT ON REACTION OF OXYGEN WITH ACETYLENE

Temp., °C.	Moles passed X 10^3 C_2H_2	Moles passed X 10^3 O_2	Moles formed X 10^3 CO	Moles formed X 10^3 CO_2	Moles formed X 10^3 H_2	Moles formed X 10^3 HCOOH + HCHO	HCOOH alone	Av. time of contact, sec.
278	8.9	8.9	038	010	0.065	044		200
278	8.9	8.9	0 57	075	.082	0.57		
% of total carbon passed			2 67	49		2 8		
278	17.8	17.8	0.13	.037	035	0.44		100
278	17.8	17.8	22	.048	078	0 51		
% of total carbon passed			49	.12		1 33		
278	356	35.6	.16	0	052	0.35		50
278	35.6	35.6	.12	.016	.013	033		
% of total carbon passed			20	.01		0 48		
310	8.9	8.9	2.54	.54	.29	1.18		200
310	8.9	8.9	2.90	61	.30	.	0 88 (50.3%)	
% of total carbon passed			15.3	3 0		6 7	4 9	
310	17 8	17.8	3.07	0.59	.29	1.72		100
311	17.8	17.8	4.78	066	.40		1 09 (52.4%)	
% of total carbon passed			11.0	1.81		4 8	3.1	
310	35.6	35.6	1.24	0.33	.18	1.89		50
313	35.6	35.6	1.62	.45	.21		0.95 (46%)	
% of total carbon passed			201	.55		265	1.33	

the time of contact: either the induction period is different for different products, or the analyzed reaction products are not all due to the primary reaction. If this latter assumption is accepted, one can deduce further that the condensable substances, and possibly hydrogen, are the first products of the oxidation (or decomposition) of acetylene, while carbon monoxide and dioxide result from secondary decompositions or oxidation of these products. Although on first glance the results at 310°, Table II, seem to differ greatly from those at 278°, in reality they agree quite well. At 310°, 30% of the acetylene reacts during the longest contact time, and since the reaction velocity depends strongly on the acetylene concentration (see below), the velocity must decrease during the reaction period owing to consumption of acetylene in the reaction. On further decrease of contact time to fifty seconds the influence of the induction period overweighs that of the consumption of acetylene, and a general decrease in the reaction velocity is observed. The data in Table II show that the yields of carbon monoxide and dioxide decrease more rapidly with the contact time than do the other reaction products; in fact, the yield of condensable substances even increases slightly.

A decrease in the contact time has little effect on the absolute amount and the weight concentration of formic acid. The increase in the total amount of oxidizable matter in the condensate shows that with decreasing contact time the amount of water present must decrease, whereas the aldehyde fraction must increase. Indeed, the iodine determination of aldehydes carried out on a sample obtained with fifty seconds' contact time yielded 30% of aldehydes in the condensate as compared with 9% obtained with 200 seconds' contact time.

The influence of gas composition on the reaction velocity was established by runs made with gases composed of 75% acetylene, 25% oxygen and 25% acetylene, 75% oxygen. These runs, which are presented in Table III, show that the reaction velocity falls off very rapidly with decreasing acetylene–oxygen ratio. The variation in reproducibility of the experiments makes uncertain any conclusions as to whether all reaction products decrease in this same ratio or not. The average decrease of two main products, carbon monoxide and the condensable matter, is about ten-fold for a change of composition from 75 acetylene–25 oxygen to 25 acetylene–75 oxygen, or a three-fold change of each of the reactants. This makes it probable either that the reaction velocity is proportional to the square of acetylene concentration, or that it is proportional to its first power and is retarded by oxygen. Runs were made with a gas mixture containing 25% acetylene and 75% oxygen in one case and 75% of air in the other case to decide between these two possibilities. These runs are presented in Table III, Series B, which shows that notwithstanding a five-fold change in oxygen concentration, the reaction velocity is not greatly changed. As a slight increase in the reaction velocity in the mixture containing air can be observed, it appears probable that oxygen has only a slight retarding influence. Accordingly, to account for the results given in Table III, one must assume that the reaction velocity is proportional to the square of the acetylene concentration and is very slightly retarded by oxygen.

TABLE III

EFFECT OF CONCENTRATION OF REACTANTS ON REACTION OF OXYGEN WITH ACETYLENE

Average time of contact, 200 seconds

Series	Temp., °C.	Moles passed × 10^3			Moles formed × 10^3			
		C_2H_2	O_2	N_2	CO	CO_2	H_2	HCOOH + HCHO
A	278	13.35	4.45	...	1.34	0.233	0.14	1.100
	279	13.35	4.45	...	1.16	.244	.13	1.170
	277	4.45	13.35	...	0.12	.042	.02	0.095
	278	4.45	13.35	...	.07	.030	.02	.157
B	296	4.45	1335	...	.39	.138	.04	.433
	296	4.45	2.67	1.068	.60	.112	.03	.485

To study the influence of the walls of the reaction vessel on the reaction velocity, a pyrex tube was filled with broken pyrex glass of a size between 6- and 14-mesh. The surface in this vessel was increased many-fold and the average diameter of the free spaces was reduced from 20 mm. in the open vessel to 1 mm. or less. Considerable difficulty was experienced at the beginning of these experiments from an inconstancy of the reaction velocity. Table IV presents two consecutive series of experiments and shows that a prolonged exposure of the vessel to the acetylene–oxygen mixture results in a decreasing reaction rate. An attempt to produce more constant conditions was made by treating the packed vessel with a normal solution of sodium chloride, washing once with distilled water, and drying. Pease[2] has observed in oxidation of other hydrocarbons using potassium chloride on glass that the salt treatment of the glass surface brought about a marked decrease in reaction velocity. Our treatment with sodium chloride did not have such an effect. The reaction velocity was speeded up slightly and was more reproducible. The absence of a lasting effect of sodium chloride is not astonishing because the glass surface in both the treated and untreated vessels became coated with a thin deposit of carbon, which was in contact with the acetylene-oxygen mixture. Table V presents the data obtained with the coated vessel and an equimolal mixture of acetylene and oxygen. The remarkable feature of the experiments is that they indicate a reaction velocity in the packed vessel many-fold slower than in the empty one. Thus at 315° some 30% of acetylene reacted in the empty vessel, whereas in the packed tube the reaction amounted to only 3 to 4%. At the same time the course of reaction is profoundly changed; the main products are now carbon dioxide and water. Increase in the amount of water in the reaction products was established by weighing the cooled trap before and after several runs. The change in the course of the reaction is manifest also from experiments on the influence of the time of contact and of the composition of the gas mixture on the reaction velocity. These data are presented in Table VI, Series A and B.

It is apparent from these experiments that the induction period characterizing the reaction in the unpacked vessel has disappeared. The velocity of reaction is now approximately independent of the time of contact and no distinct difference can be observed in the behavior of the various products of reaction. Accordingly there are no grounds to assume now that carbon monoxide and carbon dioxide are products of secondary reactions, as there were in the case of the unpacked vessel where the primary reaction led to the formation of "condensable substances." Series B, Table VI, shows the influence of the composition of the gas mixture on the reaction velocity. Variations in the compositions of the gas mixture leave the reaction velocity almost unchanged. Mixtures rich in acetylene show a somewhat higher

TABLE IV

DATA ON REACTION OF OXYGEN WITH ACETYLENE IN VESSEL OF 24-MM. INTERNAL DIAMETER PACKED WITH PYREX GLASS, 6- TO 14-MESH

Average time of contact, 200 seconds

Temp., °C.	Moles passed X 10^3		Moles formed X 10^3			
	C_2H_2	O_2	CO	CO_2	H_2	HCOOH + HCHO
256	8.9	8.9	0.110	0.22	0.020	0.0
280	8.9	8.9	.083	.25	.013	.030
315	8.9	8.9	.148	.42	.013	.045
338	8.9	8.9	.343	.93	.039	.081
355	8.9	8.9	.283	1.08	.043	.036
356	8.9	8.9	.435	1.30	.057	.126
335	8.9	8.9	.320	0.63	.043	.121
315	8.9	8.9	.410	.29	.043	.054
297	8.9	8.9	..	.22	..	.054
275	8.9	8.9	..	.05	..	.027
250	8.9	8.9	.048	.03	.009	.018

TABLE V

DATA ON REACTION OF OXYGEN WITH ACETYLENE IN VESSEL OF 24-MM. INTERNAL DIAMETER, PACKED WITH PYREX GLASS, 6- TO 14-MESH, AND TREATED WITH 1 NORMAL SODIUM CHLORIDE SOLUTION

Average time of contact, 200 seconds

Temp., °C.	Moles passed X 10^3		Moles formed X 10^3			
	C_2H_2	O_2	CO	CO_2	H_2	HCOOH + HCHO
256	8 9	8.9	0.04	0.02	002	0.01
277	8.9	8.9	.12	.04	.02	
277	8.9	8.9	.05	.08	.02	
297	8.9	8.9	.06	.12	.01	...
315	8.9	8.9	.10	.52	.01	.01
316	8.9	8.9	.10	.32	.01	...
337	8.9	8.9	.56	1.77	.06	.06
352	8.9	8.9	.74	2.70	.09	.05
354	8.9	8.9	.68	2.26	.08	.06

TABLE VI

EFFECT OF CONCENTRATION OF REACTANTS AND OF TIME OF CONTACT ON REACTION OF OXYGEN WITH ACETYLENE IN A CYLINDRICAL VESSEL OF 22-MM. INTERNAL DIAMETER PACKED WITH PYREX GLASS, 6- TO 14-MESH, AND TREATED WITH 1 NORMAL SODIUM CHLORIDE SOLUTION

Series	Temp., °C.	Moles passed × 10^3 C_2H_2	O_2	N_2	Moles formed × 10^3 CO	CO_2	H_2	HCOOH + HCHO	Av. time of contact, sec.
A	317	8.9	8.9	..	0 260	0 76	0.026	0.135	200
	316	8.9	8.9	..	.220	.56	.022	.063	
	316	17.8	17.8	..	.210	.62	.035	.140	100
	316	35.6	35.6	..	.305	.55	.052	.067	50
B	316	8.9	26.7	..	.148	.48	.017	.063	100
	316	8.9	26 7	..	.218	5 4	.0	.036	
	316	26.7	8.9	..	.235	.54	.035	.166	100
C	316	8.9	5.3	21.4	..	.14	..	.018	100

rate, but the increase is much less than the ten-fold change observed in the unpacked vessel. This means that the reaction velocity is no longer proportional to the square of the acetylene concentration. The experiment of Series C, Table VI, in which a part of the oxygen was replaced by nitrogen, shows further that the rate, instead of being weakly inhibited by oxygen, now is more or less proportional to the oxygen concentration.

Discussion of Experimental Results

A comparison of the reaction rates in packed and unpacked vessels shows that the oxidation of acetylene under the conditions employed here is a homogeneous gas reaction. An increase in the glass surface does not increase the rate; instead, such an increase of the surface decreases the reaction rate many-fold. It has been shown by Pease,[2] Hinshelwood and Thompson,[13] and Semenoff[5] that this behavior characterizes chain reactions. The abnormal dependence on the concentration of the reactants is further evidence favoring the chain character of the reaction. Oxygen, which must enter the reaction mechanism, not only does not favor the reaction but even slightly inhibits it. Such behavior is incomprehensible from the point of view of classical chemical kinetics.

The analysis of the oxidation products shows glyoxal, formaldehyde and formic acid, aside from gaseous products. It is obvious that the formation of glyoxal must precede the formation of formaldehyde and formic acid in a stepwise oxidation. The change in the amounts of glyoxal, formaldehyde and formic acid with contact time demonstrates clearly the stepwise character of the oxidation which has already been suggested by Bone.[6] However, we do not consider his scheme correct in detail. Instead of a primary product containing two hydroxyl groups, a substance of the same total composition, $C_2H_2O_2$, but consisting of two aldehyde groups, namely glyoxal, is obtained.

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[13] Hinshelwood and Thompson, *Proc. Roy. Soc. (London)*, 118A, 170 (1928).

There is a variety of possible reactions which glyoxal may undergo under our experimental conditions. Since reactions involving more than two molecules simultaneously are kinetically less probable than bimolecular and unimolecular processes, we can limit our discussion to the latter.

$$\begin{array}{lll}
\mathrm{CHO{-}CHO} & \longrightarrow \mathrm{CO} + \mathrm{HCHO} & (1)\\
\mathrm{CHO{-}CHO} & \longrightarrow 2\mathrm{CO} + \mathrm{H_2} & (2)\\
\mathrm{CHO{-}CHO} + \mathrm{O_2} & \longrightarrow \mathrm{CO_2} + \mathrm{HCOOH} & (3)\\
\mathrm{CHO{-}CHO} + \mathrm{O_2} & \longrightarrow \mathrm{CO} + \mathrm{O} + \mathrm{HCOOH} & (4)\\
\mathrm{CHO{-}CHO} + \mathrm{O_2} & \longrightarrow \mathrm{CO} + \mathrm{CO_2} + \mathrm{Hz0} & (5)
\end{array}$$

Our experiments enable us to distinguish between the relative importance of these reactions. Reaction 3 certainly does not take place to any considerable extent, for otherwise a much larger relative yield of carbon dioxide would be obtained than was actually observed. Reaction 2 cannot be predominant because only small quantities of hydrogen were obtained throughout. On the other hand, the fact that the hydrogen yield decreased only slowly on decrease of the contact time makes it probable that it is this reaction and not a decomposition of formaldehyde or formic acid that produces hydrogen. Bone maintains that hydrogen in the reaction products is due to a reaction of the type, $\mathrm{HCOOH} \longrightarrow \mathrm{H_2} + \mathrm{CO_2}$, but our experiments point strongly against this inasmuch as they show that, on variation of the contact time, the yields of carbon dioxide and of hydrogen are quite different. Accordingly Reaction 2 may be considered as playing a secondary role in the reaction sequence. Bone attributes the formation of formic acid to a secondary oxidation of formaldehyde only. Our experiments are not conclusive enough to decide whether Reaction 4 or the process $\mathrm{HCHO} + \mathrm{O_2} \longrightarrow \mathrm{HCOOH} + \mathrm{O}$ produces formic acid. In both cases one would expect decreasing yields of acid when the time of contact is decreased, but Reaction 4 would lead to a slower decrease than its formation in the oxidation of formaldehyde. A slight decrease in the amount of formic acid was actually observed; this might be construed as showing the occurrence of Reaction 4. A final decision will be possible only after a more detailed study of the yields of formic acid and formaldehyde.

The occurrence of Reaction 5 is also uncertain at present. The fact that the yields of carbon dioxide and water both decrease rapidly on shortening the contact time speaks in favor of our theory of the formation of these stable reaction products in some later stages of the reaction sequence, perhaps in the decomposition or oxidation of formic acid. The origin of carbon monoxide in the reaction is probably due to several processes. Its main source, especially at the lower temperatures, is Reaction 1. At higher temperatures additional sources of carbon monoxide may be the reactions

$$\begin{array}{l}
\mathrm{HCHO} \longrightarrow \mathrm{H_2} + \mathrm{CO}\\
\mathrm{HCOOH} \longrightarrow \mathrm{CO} + \mathrm{H_2O}
\end{array}$$

The experiments in the packed vessel show that an increase in the glass surface changes the kinetics and the entire course of the reaction. It appears that a heterogeneous oxidation of acetylene directly to carbon dioxide and water, which was quite subordinate in the unpacked vessel, has been sufficiently accelerated to overshadow the homogeneous reaction. The fact that the glass surface has a profound influence on the yield of carbon dioxide is in favor of this explanation.

A problem which remains to be discussed is the coördination of the chemical side of the processes involved in the oxidation of acetylene with the chain character of the reaction and with the kinetic relations observed. Since none of the reactions are reversible under the experimental conditions and glyoxal appears in only small quantities, it must be the primary process of oxidation of acetylene that is the rate-determining process, namely, $C_2H_2 + O_2 = C_2H_2O_2$.

Accordingly one would expect the reaction rate to be proportional to the product of the concentration of acetylene and oxygen, but this is not the case. The reaction rate is proportional to the square of the acetylene concentration and is practically independent of oxygen. Furthermore, the reaction exhibits an induction period. Similar characteristics have been observed by Thompson and Hinshelwood[4] in the oxidation of ethylene. These authors' explanation of the reaction order is essentially this: a molecule resulting from addition of oxygen to ethylene will collide with a molecule of either ethylene or oxygen; the collision with ethylene is favorable to the propagation of a reaction chain while the collision with oxygen puts an end to further chemical processes. This scheme expressed kinetically yields the experimental order. Our results with acetylene can be interpreted in the same manner. The formation of glyoxal, being an addition reaction, must take place through a three-body collision.[14] A formal agreement with experiment is obtained if it is assumed that only with acetylene as the third body is glyoxal formed, while the action of oxygen is different. It is astonishing that glyoxal is formed at all as a primary product because the direct formation of carbon monoxide and formaldehyde, $C_2H_2O_2 = CO + HCHO$, being also highly exothermic, does not need a three-body collision and therefore should occur much more readily.

The presence of reaction chains has been shown, but their mechanism remains at present uncertain. The deduction can only be made from the existence of the induction period that the presence and further oxidation of intermediary products speed up the primary oxidation of acetylene. It is quite possible that free oxygen atoms resulting in some of the single reaction steps discussed above play an important role in the reaction.

Summary

Experiments are described that show that the thermal oxidation of acetylene by oxygen can be conveniently studied in pyrex vessels between

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[14] Born and Franck, *Z. Physik*, 31, 411 (1925).

250 and 315°. A comparison of the reaction rates in packed and unpacked vessels shows not only that the reaction is homogeneous but that it is of the chain type.

The change in composition of the condensable reaction products with time of contact shows that the oxidation proceeds through the stages glyoxal–formaldehyde–formic acid. The gaseous products consist mainly of carbon monoxide, together with carbon dioxide and hydrogen. A study of the change in gas composition with contact time indicates that carbon monoxide originates mainly from the direct decomposition of glyoxal, and that carbon dioxide is due to oxidation or decomposition of formic acid, whereas the origin of the traces of hydrogen is at present uncertain.

The velocity of reaction is proportional to the square of the acetylene concentration and is independent of the oxygen concentration.

In packed vessels the homogeneous oxidation is almost entirely suppressed, and a heterogeneous oxidation of acetylene on the glass surface directly to carbon dioxide and water takes place. The rate is roughly proportional to the first power of the acetylene and oxygen concentrations. The mechanism of the reaction has been discussed.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE PHYSICS DEPARTMENT, ALABAMA POLYTECHNIC INSTITUTE]

A MAGNETO-OPTIC METHOD OF CHEMICAL ANALYSIS

BY FRED ALLISON AND EDGAR J. MURPHY

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This paper reports some results of a method which promises to be of value as a new means of chemical analysis. It also suggests a new angle of approach to certain aspects of the problem of ionization in liquids. The method is a refinement of one previously described by Allison[1] in the investigations of the time lag differences of the Faraday effect behind the magnetic field in certain liquids as a function of the wave length of the light used.

In a study of solutions it was subsequently found that each chemical compound, regardless of the presence of other substances, produces its characteristic minimum (or minima) of light intensity, which persists until the concentration is reduced to about 1 part in 10^{11}.[2] This fact suggested that the method might have application in some cases of chemical analysis.

The authors[3] have extended these findings of Allison to include a rather comprehensive series of solutions of chlorides, nitrates, sulfates and hydroxides.

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[1] Allison, Phys. *Rev.*, 30, 66 (1927).

[2] Allison, *ibid.*, 31, 313 (1928).

[3] Allison and Murphy, *ibid.*, 35, 124 (1930).

The experimental arrangement is diagrammatically shown in Fig. 1. The apparatus together with its manipulation has already been described.[1,2,3] A kenetron tube K replaces the Wehnelt interrupter of the original set-up, the condenser C being charged from the high voltage side of the transformer M. Sliding rheostats R_1 and R_2 are in series with the primaries of the main transformer and the filament transformer, respectively. B_1 and B_2 represent the cylindrical cells which are placed co-axially within the helices of wire, N_1 and N_2 the polarizing and analyzing Nicol prisms, L a converging lens, F Wratten filters and T_1T_1 and T_2T_2 the sliding trolleys. A steady source of light in connection with a monochromator has at times been used instead of the spark A, the latter being screened.

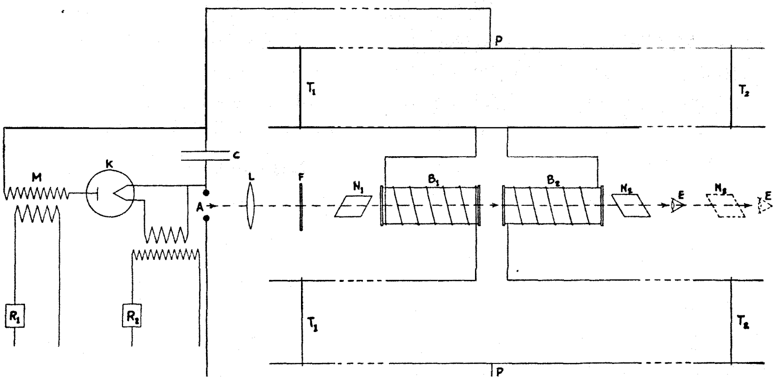

Fig. 1.—Diagram of apparatus and connections.

For some time we have often found convenient a combination of the air or light path and the wire path in measuring these time effects. The sliding trolley, although itself equipped with a vernier, becomes the coarser scale, while the finer settings are made by displacing the cell B_2 by means of a rack and pinion motion. The trolley is first set at a point within a few centimeters of the position at which a minimum is observed and the minimum is then finally located with surprising precision on the rack and pinion scale. The wire and light paths are then simply combined.

Representative results are given in Table I. The compounds of each series are arranged in columns in the order of the increasing chemical equivalents of their metallic elements. In the first column under each compound are recorded the positions of the characteristic minima of the compound as read on the wire path scale. In the second columns are tabulated the differential time lags, all of which are with reference to carbon bisulfide. The zero of the wire path scale is at 15.00. The differential lags are therefore found by subtracting the scale readings of the minima from this zero point, since the scale is laid off in units of 30 cm. The lags are thus

TABLE I

SCALE READINGS OF CHARACTERISTIC MINIMA AND DIFFERENTIAL TIME LAGS WITH REFERENCE TO CARBON BISULFIDE

Scale reading	Seconds $\times 10^{-9}$	Scale reading	Seconds $\times 10^{-9}$	Scale reading	Seconds $\times 10^{-9}$	Scale reading	Seconds $\times 10^{-9}$
HCl		HNO_3		H_2SO_4		HOH	
15.85	−0.85	5.50	9.50	8.43	6.57	9.30	5.70
15.95	− .95	5.61	9.39	8.65	6.35		
$LiCl$		$LiNO_3$		Li_2SO_4		$LiOH$	
16.22	−1.22	5.85	9.15	9.00	6.00	10.03	4.97
16.45	−1.45	5.95	9.05	9.10	5.90	10.18	4.82
$AlCl_3$		$Al(NO_3)_3$		$Al_2(SO_4)_3$		$Al(OH)_3$	
16.58	−1.58	6.10	8.90	9.66	5.34	10.37	4.63
$MgCl_2$		$Mg(NO_3)_2$		$MgSO_4$		$Mg(OH)_2$	
16.82	−1.82	6.20	8.80	10.04	4.96		
16.90	−1.90	6.25	8.75	10.40	4.60		
17.03	−2.03	6.30	8.70	10.62	4.38		
NH_4Cl		NH_4NO_3		$(NH_4)_2SO_4$		NH_4OH	
17.82	−2.82	6.80	8.20	11.21	3.79	11.05	3.95
$FeCl_3$		$Fe(NO_3)_3$		$Fe_2(SO_4)_3$		$Fe(OH)_3$	
17.96	−2.96	6.83	8.17	11.32	3.68	11.60	3.40
18.05	−3.05	6.90	8.10	11.45	3.55	11.74	3.26
$CaCl_2$		$Ca(NO_3)_2$		$CaSO_4$		$Ca(OH)_2$	
18.44	−3.44	7.17	7.83	11.54	3.46	12.37	2.63
18.66	−3.66	7.20	7.80	12.05	2.95	12.57	2.43
$NaCl$		$NaNO_3$		Na_2SO_4		$NaOH$	
18.73	−3.73	7.21	7.79	13.00	2.00	13.47	1.53
$AsCl_3$		$As(NO_3)_2$		$As_2(SO_4)_3$		$As(OH)_3$	
18.98	−3.98			13.17	1.83		
$CrCl_2$		$Cr(NO_3)_2$		$CrSO_4$		$Cr(OH)_2$	
19.15	−4.15	6.50	8.50				
$MnCl_2$		$Mn(NO_3)_2$		$MnSO_4$		$Mn(OH)_2$	
19.22	−4.22	7.29	7.71	13.67	1.33	13.95	1.05
$FeCl_2$		$Fe(NO_3)_2$		$FeSO_4$		$Fe(OH)_2$	
19.25	−4.25			13.90	1.10		
19.40	−4.40			14.20	0.80		
$CoCl_2$		$Co(NO_3)_2$		$CoSO_4$		$Co(OH)_2$	
20.15	−5.15	7.30	7.70	14.40	0.60	14.74	0.26
$NiCl_2$		$Ni(NO_3)_2$		$NiSO_4$		$Ni(OH)_2$	
20.30	−5.30	7.31	7.69	14.52	0.48	15.28	−0.28
20.40	−5.40	7.34	7.66	14.66	.34	15.60	− .60

TABLE I (*Continued*)

Scale reading	Seconds × 10^{-9}	Scale reading	Seconds × 10^{-9}	Scale reading	Seconds × 10^{-9}	Scale reading	Seconds × 10^{-9}
$CuCl_4$		$Cu(NO_3)_2$		$CuSO_4$		$Cu(OH)_2$	
20.48	−5.48	7.40	7.60	14 80	0.20	10.04	−1.04
20 68	−5 68	7.43	7.57	15.00	.00	16.35	−1.35
$ZnCl_2$		$Zn(NO_3)_2$		$ZnSO_4$		$Zn(OH)_2$	
21.08	−6.08	7.54	7.46	15 21	−0.21	16.27	−1.27
21.40	−6.40	7.56	7.44	15.42	− .42	16 52	−1.52
21.73	−6.73	7.67	7.33	15.75	− .75	16.93	−1.93
21.85	−6.85	7.70	7.30	16.03	−1.03	17.20	−2.20
KCl		KNO_3		K_2SO_4		KOH	
22.50	−7.50	7.82	7.18	16.74	−1.74	19.54	−4 54
22.87	−7.87	7.84	7.16	16.98	−1.98	19.95	−4.95
$SbCl_3$		$Sb(NO_3)_3$		$Sb_2(SO_4)_3$		$Sb(OH)_3$	
23.30	−8.30			17.96	−2.96	19.65	−4.65
23.66	−8.66			18.13	−3.13	19.90	−4.90
$SrCl_2$		$Sr(NO_3)_2$		$SrSO_4$		$Sr(OH)_2$	
24.35	−9.35	8.00	7.00			20.33	−5.33
24.59	−9.59	8.30	6.70			20.92	−5.92
$CdCl_2$		$Cd(NO_3)_2$		$CdSO_4$		$Cd(OH)_2$	
25.06	−10.06			18.50	−3.50		
25.28	−10.28			18.68	−3.68		
25.54	−10.54			18.81	−3.81		
25.90	−10.90			19.00	−4.00		
26.10	−11.10			19.17	−4.17		
26.25	−11.25			19.48	−4.48		
$SnCl_2$		$Sn(NO_3)_2$		$SnSO_4$		$Sn(OH)_2$	
27.40	−12.40	8.70	6.30	20.10	−5.10		
27.58	−12.58	8.74	6.26	20.40	−5.40		
27.88	−12.88	8.80	6 20	20.62	−5.62		
28.25	−13.25	8.83	6.17	21.00	−6.00		
28.54	−13.54	8.88	6.12	21.27	−6.27		
28.82	−13.82	8.90	6.10	21.40	−6.40		
29.23	−14.23	8.95	6.05	21.80	−6.80		
29.55	−14.55	9.00	6.00	22.06	−7.06		
29.80	−14.80	9.12	5.88	22.54	−7.54		
30.10	−15.10	9.21	5.79	22.81	−7.81		
30.30	−15.30	9.28	5.72	23.22	−8.22		
CuCl		$CuNO_3$		Cu_2SO_4		CuOH	
30.38	−15.38	9.35	5.65				
30.68	−15.68	9.50	5.50				
$BaCl_2$		$Ba(NO_3)_2$		$BaSO_4$		$Ba(OH)_2$	
30.80	−15.80	9.45	5.55	23.55	−8.55		
31.18	−16.18	9.50	5.50	23.78	−8.78		
31.35	−16.35	9.58	5.42	23.98	−8.98		
31 65	−16.65	9.72	5.28	24.20	−9.20		

TABLE I *(Concluded)*

Scale reading	Seconds $\times 10^{-9}$	Scale reading	Seconds $\times 10^{-9}$	Scale reading	Seconds $\times 10^{-9}$	Scale reading	Seconds $\times 10^{-9}$
$PbCl_2$		$Pb(NO_3)_2$		$PbSO_4$		$Pb(OH)_2$	
36.90	−21.90	9.95	5.05	23.82	−8.82	19.18	−4.18
37.07	−22.07	10.08	4.92	24.36	−9.36	19.44	−4.44
37.30	−22.30	10.30	4.70	24.72	−9.72	19.65	−4.65
37.68	−22.68	10.46	4.54	25.10	−10.10	19.86	−4.86
AgCl		$AgNO_3$		Ag_2SO_4		AgOH	
38.65	−23.65	10.60	4.40	26.17	−11.17		
39.18	−24.18	10.80	4.20	26.82	−11.82		
HgCl		$HgNO_3$		Hg_2SO_4		HgOH	
40.10	−25.10	10.82	4.18	27.75	−12.75	19.40	−4.40
40.42	−25.42	10.93	4.07	28.04	−13.04	19.60	−4.60
40.86	−25.86	11.01	3.99	28.30	−13.30	19.74	−4.74
41.12	−26.12	11.16	3.84	28.66	−13.66	20.00	−5.00
41.34	−26.34	11.28	3.72	29.06	−14.06	20.37	−5.37
41.65	−26.65	11.42	3.58	29.48	−14.48	20.70	−5.70
42.10	−27.10	11.52	3.48	29.88	−14.88	20.96	−5.86
TlCl		$TlNO_3$		Tl_2SO_4		TlOH	
42.65	−27.65	11.15	3.85	30.20	−15.20	21.40	−6.40
42.95	−27.95	11.40	3.60	30.30	−15.30	21.70	−6.70

computed on the assumption that the electric surges in the wires travel with the speed of light, because in practice it is more convenient with a given set-up to adhere strictly to the readings on the wire path scale and because we no longer find it worth while to check the readings on the light path scale. There has not been opportunity, for lack of both time and material, to locate the minima corresponding to those compounds for which no values appear in the table. Some salts, such as cuprous nitrate and stannous nitrate, were obtained by the addition of the corresponding acid to dilute solutions of the chlorides. We are publishing data for only such hydroxides as we have been able to procure, though we do find in general the hydroxides present when the salts of the metals are in solution.

Since the position of each minimum corresponding to a compound is tabulated in terms of a scale whose units are marked off in lengths of 30 cm., which in time units have the value of 10^{-9} sec., the second decimal refers to a length of 3 mm. or a time of 10^{-11} sec. The various regions of the scale occupied by the nitrates, hydroxides, sulfates and chlorides will be noted from the data of the table. The chlorides have the advantage of what may be termed greater resolving power in the location of minima. In seeking to determine the presence of a metal, a very valuable check is afforded by observing the minima corresponding to each of the four compounds. There are overlapping regions, as will be seen from a study of the table, but when one gains familiarity with the order in which the minima occur, there is little ground for confusion. It should be kept in mind that these time intervals recorded are differential, the time lag for each compound being with reference to carbon bisulfide. (Other liquids than carbon bisulfide have been used in cell B_1. When this is done the characteristic minima due to compounds in B_2 fall at different parts of the scale in consistent agreement with the differential time lag between the new liquid in B_1 and carbon bisulfide.)

After reading the minima of a number of compounds, it appeared upon a study of the results that the positions of the minima were functions of the atomic weights of the metallic elements of the compounds or, more precisely, of the atomic weights divided by the valence, that is, the chemical equivalents. In other words, the differential time lag in general decreases with increasing chemical equivalent. In each of the four series of compounds of Table I the longest differential lag is thus produced by the compounds of hydrogen, the shortest by those of thallium. Furthermore, elements which have two different valences exhibit as a rule two minima, or two series of minima, in different regions of the scale corresponding to the chemical equivalents in the two cases, the number of minima being the same for each valence. Cases of more than two valences have not been studied. There are several slight exceptions to the law of decrease of differential lags with chemical equivalence. Among these will be noted the minima of the compounds of nickel and cobalt and those of some of the heavy metals which have a number of isotopes, the minima of the latter compounds overlapping in certain regions of the scale. In reading across the table, it will be seen that for any metallic element there also exists this relationship between differential time lag and chemical equivalent in the case of the chlorides, sulfates and nitrates, the hydroxides falling somewhat out of line in this respect.

It will be further noted from the tabulated results that each compound produces either a single minimum or two or more close minima. The number of these minima, with few exceptions, is the same as the number of the known isotopes of the metallic elements of the compounds, whether the elements be in the chloride, nitrate, sulfate or hydroxide form. This is in keeping with the relationship discussed in the preceding paragraph, namely, the variation of the differential lag with atomic mass. The isotopes of the metallic element, in each series of compounds, alone seem to be operative in producing minima. Hydrochloric, nitric and sulfuric acids each produce two minima, for which we are unable to account. It will now be seen that the cobalt minimum takes its place regularly with respect to the minimum of the heavier isotope of nickel but not with respect to that of the lighter.

Several compounds at great dilution behave as if the magnetic rotation exerted by them is of negative sign. For example, repeated observations failed to reveal minima characteristic of ferric sulfate. Upon reversing the field in B_2, however, the two minima appeared in the appropriate region of the scale, as shown in the table. These results are suggestive of those reported by Roberts[4] and others concerning the magnetic rotary dispersion of certain paramagnetic solutions. It is planned to make further study of this behavior of solutions.

Since water in all the reported results was the solvent of the compounds, considerable time has been devoted to searching for minima when the purest water which we have available fills the cell B_2, namely, that distilled in quartz. There are some four or five minima distributed over the scale which we have been unable to remove by redistillations. One of these, because of its distinctness, we have attributed to water. The others we have been unable to identify. Some are doubtless due to compounds dissolved from the glass cell even during the short time the water is in contact with the glass before an observation can be made. These unknown minima, being always at fixed points of the scale, are not a source of confusion but they are actually an advantage in supplying fiducial points along the scale. It is planned to investigate further the causes of these minima.

We have thus far had the opportunity to make a study of practically no inorganic compounds except those listed in the table. A great deal of laborious observation is required to locate the characteristic minima with precision for a large series of compounds. Once the table is determined, however, it affords a rather rapid means of analysis for any compounds of the series. It is planned to construct in the near future tables for carbonates, phosphates, etc., as well as for certain organic compounds. There is reason to believe that this method is applicable to most, if not all. compounds.

The method appears to be a reliable one, as attested by a large number of successful tests and chemical analyses. Several advantages inherent in it may be suggested. One is the speed with which the presence of a compound may be detected. Another is due to the fact that the sample is not destroyed by the analysis, since it is merely subjected to the passage of a beam of light through it. Inasmuch as very small quantities are easily detectable, substances which are very slightly soluble, whether transparent or opaque, readily lend themselves to this sort of analysis. It may be further remarked that the apparatus necessary is comparatively inexpensive. Its operation, however, requires the attainment of a considerable amount of experience and technique on the part of the observer. It is not to be expected, in the present stage of development, that the method will yield dependable results in the hands of the average observer. Improvements are still being made, however, and it is hoped that ultimately it will be adapted to more general usage.

[4] R. W. Roberts, *Phil. Mag.*, 9,361 (1930).

An analogy with spectrum analysis may be of interest. Instead of spectrum lines characteristic of the chemical elements, we have disposed along a scale (some 25 feet long) the minima characteristic not of the elements alone but of the chemical compounds. For example, the various compounds of sodium, $NaCl$, $NaNO_3$, Na_2SO_4, $NaOH$, show minima in different regions of the scale, by means of which each compound when in solution may be recognized. The metallic element in the compound seems to be chiefly effective in producing minima. At any rate, we have found no minima which we could ascribe to the negative part of the molecule. Such minima, of course, may occur in the extended regions of the scale which have not been carefully explored.

Since we find it far more convenient to use the wire path method (or a combination of the wire and light paths), observations have been carried out on the three different set-ups, all built of somewhat different dimensions and in two different rooms, to determine how the positions of the minima correspond on different scales as read on the wire path scale. It is found that, when the set-ups are constructed symmetrically, there is very close agreement in the differences between corresponding minima on the three. Each new set-up, however, should have its wire path calibrated by finding the exact positions of the characteristic minima corresponding to the compounds for which analyses are subsequently to be made. The positions of the minima are not changed, within the errors of observations, by wide variations in the resistance, capacitance or inductance of the circuit, though the distinctness of the minima is affected by such changes. Optimum conditions for sharp minima may be found by experiment through the adjustments of the constants of the circuits. The beginner is likely to meet with considerable difficulty here, since he will probably fail to note the minima at all until this optimum condition is approximated. No fixed rules can be laid down for this adjustment, owing to the variations in the constants of different circuits. It is especially important that the capacity of the condenser be adjustable to the proper magnitude.

Settings on a minimum may be repeated by the same observer, or by different observers, within a deviation of a very few millimeters. Rather close minima may therefore be distinguished with considerable ease. The minima are surprisingly sharp, some more so than others. The hydroxides produce minima which are least sharp and most difficult to locate with precision,

The sensitiveness of the method has proved to be surprisingly great. Tests have been carried out on a representative number of solutions of compounds of graded concentrations. The results show that about 1 part in 10^{11} of the solvent can be detected. This is true for both organic and inorganic compounds. The minima show no appreciable change in distinctness at various stages of concentration until the dilution at which they vanish is approached, when they gradually fade out, usually between 1 part in 10^{11} and 1 part in 10^{12}. The sensitivity is not appreciably affected by the presence of other compounds in the solution, but it depends somewhat upon the observer, the chemical compound and the adjustment of the apparatus. The sensitiveness of this magneto-optic method in comparison with other methods is indicated in the following table (the data are quoted from Aston).[5]

	Mass in am. at which the method breaks down
Ordinary chemical balance	8.5×10^{-5}
Quartz micro-balance	2.58×10^{-9}
Spectrum analysis (Na lines)	3.23×10^{-10}
Ordinary microscope	6.25×10^{-13}
Ultramicroscope	2.38×10^{-18}
	5.15×10^{-22}
Magneto-optic method about	1×10^{-11}

It is recognized, of course, that the results reported in this paper cannot be accounted for on the classical theory of magneto-optics nor are they in accord with experiments on the variation of the magnetic rotation with concentration. Furthermore, our findings are difficult perhaps to reconcile with the modern theory concerning ionization in very dilute solutions. While we are as yet unable to offer a satisfactory interpretation of our results, there are several points that should be mentioned. The effect is certainly a time effect, because the characteristic minima are produced by changes in the light path alone, as well as by changes in the wire path. This is further borne out by the fact that when the two cells are exchanged, the positions of the minima are shifted to points of the scale in keeping with this interpretation. Furthermore, when a tube of water is introduced between B_1 and B_2, the position of a given minimum is displaced forward on the light path scale in proportion to the lengthening of the optical path by the water. (This is of additional interest in suggesting a new method for the direct measurement of the speed of light in transparent liquids.) In searching for oscillations several methods were employed. A test coil attached to a vacuum thermocouple was placed alternately in the helix of B_1 and B_2 and the trolleys moved along the scale. The deflecting instrument showed no indication of maxima or minima. A neon tube also failed to give such indications when moved along the scale between the trolley wires. A thermo-galvanometer connected in series with one branch of the circuit showed no maximum and minimum readings corresponding to different points of the scale as the trolley was displaced. An effort was also made to detect oscillations by resonance in a vacuum tube circuit set up for the purpose, but no oscillations capable of affecting our results could be found.

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[5] Aston, *J. Franklin Inst.*, 193, 583 (1922).

In the present light of our investigations we believe that the phenomena are most probably to be interpreted as due to differential time lags in the Faraday effect. Such an abnormal magnetic rotation in these very weak solutions may possibly be accounted for because of several factors, namely, the high frequency of the magnetic field, the enormous instantaneous amperage and the steepness of the wave front of the transient surges of current. That the form of wave front may be effective is suggested from our experience last summer, with the coming of the first rains. As our research room, situated in the basement, became more and more humid, the minima entirely disappeared, though no changes in our apparatus had been made. Corona losses were obviously rather large. We tried the expedient of bringing in several heaters, when, within a few hours, the minima were visible again. We found it necessary to control the humidity in this way throughout the summer. During nine months of the year no such control is necessary. While as pointed out above a differential Faraday time lag still seems the most plausible interpretation, the experimental results herein reported would not be undermined should this interpretation subsequently be found untenable, since these results are based upon actual measures of some time effect.

Investigations are now in progress to ascertain to what extent the method is applicable for the quantitative estimation of compounds present in extremely small amounts. The preliminary results are very encouraging. With a series of increasing and known concentrations of a given compound in water (serving as standards), observations are carried out to find at what concentration the characteristic minima of the compound first appear. Most compounds for which quantitative tests have been made reveal their presence when the concentration is near 1 part in 10^{11}. By making observations on a corresponding series of increasing concentrations of the unknown solution in water, one notes as before the concentration of the unknown solution in which the minima characteristic of the particular compound are first observed. By a simple computation the quantity of the compound in the unknown solution may then be determined. As the gradations in the increasing concentrations of the solution may be made as small as one desires, it is believed that the method has possibilities of an accuracy in quantitative analysis that will render it valuable for some purposes. In a later paper it is planned to give a more definite report on the quantitative aspects of the method.

Our recently reported evidence[6] of the presence of element 87 in certain samples of pollucite and lepidolite ores is based upon the location of minima characteristic of an element of the atomic weight and valence ascribed to eka-cesium. An additional report of this investigation is contemplated in the near future.

[6] Allison and Murphy, *Phys. Rev.*, 35, 285 (1930).

It is a pleasure to acknowledge the helpful cooperation of a number of chemists. We mention in particular our indebtedness to Dr. J. L. McGhee, of Emory University, who has contributed greatly by his collaboration in the work of chemical analysis and otherwise; to Professor H. D. Jones, formerly our colleague and at the present time an industrial chemist, who has checked some of our observations and has made analyses by the method; to our colleague, Professor H. M. Martin, whose advice in problems of inorganic chemistry has been frequently sought; in fact, to the entire faculty of chemistry in this Institution for their cordial attitude of cooperation. We wish also to express our thanks to Mr. J. H. Christensen, student assistant in physics, for taking many observations, particularly with the hydroxides, and for making a number of checks on our work.

Summary

1. Each compound studied produces its own characteristic minimum, or minima, of light, regardless of the presence of other compounds.
2. The characteristic minima of those compounds for which quantitative tests have been made do not disappear until the concentration is reduced to about one part of the compound in 10^{11} parts of water.
3. These minima appear at points along the scale in the order of the chemical equivalents of the metallic elements of the compounds, or the differential time lag is some inverse function of the chemical equivalent.
4. The number of characteristic minima, with few exceptions, is equal to the number of known isotopes of the metallic element of the compound.
5. The method promises to be of value in quantitative as well as in qualitative analysis in work dealing with very small quantities of materials.

AUBURN, ALABAMA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 188]

HEATS OF NEUTRALIZATION BY THE CONTINUOUS FLOW CALORIMETER

BY LOUIS J. GILLESPIE, RAYMOND H. LAMBERT AND JOHN A. GIBSON, JR.

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The continuous flow calorimeter[1] served to locate a serious error in an accepted value[2] for the heat of neutralization of sodium hydroxide with hydrochloric acid, in agreement with the findings of Richards and Rowe,[3] which were published at the same time. Richards and his collaborators at Harvard have given a large body of data which seem to be of high precision, and repetition or extension of their measurements appears pointless

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[1] Keyes, Gillespie and Mitsukuri, THIS JOURNAL, 44, 707 (1922).

[2] Wörmann, Ann. *Physik,* [4] 18, 775 (1905).

[3] Richards and Rowe, THIS JOURNAL, 44,684 (1922).

unless the chemicals used, especially the alkalies, are pure to within about 0.1 Now the continuous flow calorimeter demands large supplies of carefully controlled solutions. Furthermore, it furnishes merely temperature changes and cannot be used alone, therefore, to extend the data of Richards and his collaborators into temperature regions where no specific heat data exist. We have been forced to limit our efforts to verification of some of the results of Richards and his collaborators at the temperature of their experiments, and to test the applicability of the Kirchhoff equation[4] by a few direct measurements at other temperatures.

We supposed at first that we should be able to check the work of the Harvard investigators only with respect to the temperature changes due to the reactions, but found that enough experimental work was available by other workers to furnish independent specific heats, and therefore afford heats of reaction completely independent of the Harvard work.

The apparatus and method used were essentially the same as that of Keyes, Gillespie and Mitsukuri, with minor improvements of the method of controlling the speed of flow and with one change of technique which enabled the rise of temperature to be obtained at unusually slow rates of flow.

When the rate of flow is too small, the mixing at the double concentric nozzles is imperfect when the average effluent is neutral, but may be good enough when the average effluent is either acid or alkaline. It was found possible at such a rate of flow to determine the rise of temperature for a neutral effluent by plotting the change of temperature against excess of acid or of alkali as indicated by neutralizing 100 cc of effluent. Excess of alkali was plotted as negative excess acid, and two intersecting straight lines were used to smooth the observations and to find the maximum rise of temperature.

Platinum thermometry was used as before. The two thermometers were tested from time to time for the fundamental interval and the delta value. It was necessary to have a new calorimeter constructed, and the inside of the Dewar space was silvered. The silvering reduced the heat loss considerably. The small difference in indication of the two thermometers was rendered of no influence by determining the difference of readings when pure water was run through both sides of the apparatus; it was found possible to set the temperature of the preliminary thermostat at such a value that the difference of readings was practically independent of the rate of flow within the necessary range, and this adjustment was made and the difference determined for each experiment. This difference was then applied as a correction to one thermometer, thus basing all temperatures on the indications of a single thermometer.

Chemicals Used. Ordinary distilled water of good quality was used. A good grade of hydrochloric acid was made up to constant boiling composition and distilled into three fractions. The middle third was further divided into three portions by distillation and the middle third kept. It was standardized gravimetrically by the silver chloride method. A precision within 0.1% was apparently obtained. The results were satisfactorily checked by reference to recrystallized acid potassium phthalate. Fresh solutions were used, though the carboy in which they were kept had been used for years to hold hydrochloric acid and tests of the acid by acidimetric titration and by the silver chloride method showed no change of the acid on standing even for several weeks.

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[4] When approximately integrated

The alkalies were standardized acidimetrically by reference to the acid, using weight burets.

The carbonate content was determined by first passing acid into base in the presence of carbon dioxide-free air. Secondly, base was added to a new portion of the acid in a stream of carbon dioxide-free air.

A good grade of potassium hydroxide from alcohol was dissolved in water and freed from carbonate in the apparatus of Knobel,[5] who very kindly lent us his apparatus. In this apparatus potassium amalgam is formed by electrolysis in one of two flasks which communicate at the bottom under mercury, and decomposed by distilled water in the other. The resulting solution contained only 0.05 mole of potassium carbonate per hundred moles of total alkali.

For sodium hydroxide the apparatus was not suitable. An initial phase of sodium amalgam reacted very slowly and appeared unstable. After some time a new phase seemed to appear that would hardly react with water, so that sufficient hydroxide could not be obtained for an experiment even after a week of electrolysis. Hence, from sodium hydroxide partially freed from carbonate by sedimentation from a concentrated solution, a viscous amalgam was formed by electrolysis. This was washed many times with cold conductivity water and placed in a large bottle, the amalgam filling about one-fourth the volume of the bottle. Steam was then passed through the amalgam. The hot water reacted rapidly with it. By the time the bottle was filled with condensed liquid, sufficient alkali had been formed to make a strong solution. After the washing with conductivity water the operations were carried out in the absence of carbon dioxide. The solution contained less than 0.2 mole of sodium carbonate per hundred moles of total alkali.

Unfortunately such alkali was not available for all of the experiments and in such a case sodium hydroxide freed from carbonate by sedimentation was used. Owing in part to the large volumes taken. this method was not uniformly successful and the solutions used for the experiments contained sometimes more carbonate than is desirable in a precision experiment.

The Specific Heats of Aqueous Solutions of Sodium Chloride and of Pofassium Chloride.—The continuous flow calorimeter gives temperature elevations to a high degree of precision and in order to calculate heats one should know the heat capacities of the products (or of the factors) of the reaction to an equal precision. In the present case the heat capacities of solutions of sodium and of potassium chloride were needed at several temperatures, and it proved necessary to construct original specific heat tables, smoothed for both temperature and concentration. Fortunately the work of Bousfield and Bousfield[6] proved to be very consistent with that of Richards and Rowe[7] at 20°, and with that of Randall and Bisson[8] at 25°, so that reliable results could be obtained without any attempt to utilize scattered data, or data without the appearance of special precision, of other investigators.

Bousfield and Bousfield[6b] determined over a series of concentrations the

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[5] Knobel, THIS JOURNAL, 45. **70 (1923).**

[6] Bousfield and Bousfield, *Trans.* Roy. *Soc. London,* **211A, 199 (1912);** (b) **218A, 119 (1919).**

[7] Richards and Rowe, THIS JOURNAL, 43, **770 (1921).**

[8] Randall and Bisson, *ibid.*, 42, **347 (1920).**

total heat in joules required to raise the temperature in steps of 13° from 0.5 to 39.5'. They had previously[ea] done the same for water. They recognized in their second paper that their values for water might be in error, and in fact they are, according to recent values of the Bureau of Standards? but they believed their results for solutions to be comparable with those for water, and this belief is borne out by the present calculations.

To deduce specific heats from their data, the total heat in joules was differentiated graphically with respect to temperature (at each concentration), and the tangent was divided by the instantaneous value of the specific heat of pure water given by their earlier experiments and expressed in their equation for J_θ (Reference 5, page 236). This gave the true specific heat referred to water at the same temperature. From the Bureau of Standards data[g] conversion factors were found by interpolation to convert specific heats in calories at t° to 20'-calories. The so-converted values were smoothed at the desired temperatures with respect to concentration, plotting the deviation from linearity of $1 - C_p$ with concentration expressed in moles of substance per mole of water, and were finally interpolated by means of the deviation plots for evenly spaced values of the concentration as well as for the particular concentrations needed for the calculation of heats.

As a check on the results at 20°, the specific heats given by Richards and Rowe[7] for both salts at 18° in 18'-calories were used to find values at 20° in 20'-calories, using smoothed temperature coefficients from the data of Bousfield and Bousfield and the conversion factors from the Bureau of Standards data. Examination of Table I, in which these Richards and Rowe values (R-R) are given together with the values from Bousfield and Bousfield (B-B), show the excellent agreement. At the concentrations at which values were needed for calculations of heats, the agreement is perfect. At 25° the deviation curve through the Bousfield data for sodium chloride passed beautifully through the two points of Randall and Bisson. Because little use was made of the excellent work of the Bousfields in the compilation of the "International Critical Tables," specific heats from their data alone are given in Table I, rather than values, possibly better, derivable from more than one source. The specific heats of sodium chloride solutions have been given by Lipsett, Johnson and Maass[10] for both 20 and 25°. Since these were determined indirectly and are not altogether independent of the values of Richards and Rowe, they were not utilized for the present comparisons.

The values at 50° were determined entirely by extrapolation without the aid of check determinations, and cannot be regarded as accurate. They are given mainly as an aid to the correction of our calculations of heats,

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[9] Osborne, Stimson and Fiock, *Mech.* Eng., 51, 125 (1929), Table 3.

[10] Lipsett, Johnson and Maass, THIS JOURNAL, 49,925, 1940 (1927).

which will be possible when accurate specific heats are determined at that temperature.

TABLE I

SPECIFIC HEATS FOR $NaCl \cdot hH_2O$ AND $KCl \cdot hH_2O$ IN 20°-CALORIES

B-B, from Bousfield and Bousfield; R-R, from Richards and Rowe

Salt	NaCl	NaCl	NaCl	NaCl	NaCl	KCl	KCl	KCl
Authors	B-B	R-R	B-B	B-B	B-B	B-B	R-R	B-B
h \ *t*	20	20	25	32	50[a]	20	20	25
10	0.7920	...	0.7921	0.7916	0.7905	...	...	...
12.5	.8144	...	.8133	.8141	.8147	...	...	...
25	.8797	0.8786	.8804	.8816	.8836	0.8328	0.8319	0.8338
50	.9302	.9286	.9314	.9318	.9324	.9035	.9036	.9045
100	.9617	.9611	.9622	.9625	.9641	.9478	.9482	.9480
200	.9796	.9794	.9797	.9799	.9819	.9726	.9729	.9723
400	.9895	.9894	.9892	.9893	.9911	.9860	.9861	.9854
800	.9946	.9946	.9943	.9943	.9957	.9929	.9930	.9924
1600	.9972	.9972	.9969	.9968	.9980	.9965	.9965	.9960
∞	1.0000	1.0000	.99959	.99943	1.00038	1.0000	1.0000	.99959

[a] Severely extrapolated.

The specific heats actually used for heat calculations were interpolated with the aid of the same deviation plots used in constructing the tables, and were found for the final concentration of the solutions and for a temperature equal to the initial temperature plus one-half the temperature rise due to the reaction. Only at 50° did it make a difference of more than one calorie in the heat whether the specific heat was calculated for this mean, or for the initial temperature. The concentration at which the specific heat was calculated was not quite the concentration of moles of NaCl (from NaOH) per mole of water, but the total moles NaCl from NaOH, NaCl from Na_2CO_3, and $NaHCO_3$ from Na_2CO_3. Here the loss of heat capacity due to the presence of $NaHCO_3$ was assumed to be the same as for NaCl, which was safe, as the total error made, if the NaCl and $NaHCO_3$ from the small concentration of Na_2CO_3 had both been neglected in the calculation of the heat capacity, would have been only 2.7 calories in the worst case. The water formed during the reaction was naturally taken into account in calculating the concentration.

The calculation of the results was in general the same as before,[1] except for some small added corrections. The effect of carbonate in the alkali was allowed for in the same way. The necessary corrections were applied to give − AH, the heat evolved at constant pressure, for the reaction

$$NaOH \cdot 0.5(h-1)H_2O + HCl \cdot 0.5(h-1)H_2O = NaCl \cdot hH_2O - AH, \text{ at } t° \qquad (1)$$

where h is the number of moles of water associated with 1 mole of salt in the product of the neutralization. Atomic weights were used as in the Harvard calculations, namely, "International Critical Tables" values with the exception that 1.008 was used for hydrogen. Consistently with their recent work, the heats are given in 20'-calories.

Since the concentrations of the acid and alkali were not identical, the results were corrected to the form of Equation 1 by the use of heats of dilution, obtained directly from the Harvard work[7,11,12] or indirectly with the aid of their recent heats of dilution and Kirchhoff's law. These corrections never exceeded **3** calories.

The treatment of the potassium chloride data was the same as for sodium chloride, and the corrections smaller.

TABLE II

RESULTS OF THE CONTINUOUS-FLOW CALORIMETRY

No. 6 is the recomputed value from the previous work[1]

No.	Salt	t	h	x	t'	$1/h'$	C_p	- AN	$-\Delta H$(R)
1	NaCl	20	1080.7	0 255	20.354	0.000930	0.9961	137%	13773
2	NaCl	20	5G6.5	.50	20.678	.001783	.9924	13803	13823
3	NaCl	24.99	1101.4	.15	25.333	.000911	.9957	13582	...
4	NaCl	32 27	568.8	.38	32 917	.001771	.9922	13211	...
5	NaCl	32 27	566 0	.20	33 953	.001774	,9922	13274	...
6	NaCl	32.3	520.5	.42	33.008	.001921	.9916	13284	...
7	NaCl	50 04	52.87	.10	57.04	.01895	.9359	13237	...
8	NaCl	50.04	99 91	.13	53.58	.01003	.9642	12676	...
9	KC1	20	547.8	.05	20.705	.001827	.9896	13864	13861

The results of the calorimetry are given in Table II. t, h and — AH refer to Equation 1; x is the number of moles of sodium carbonate or potassium carbonate per 100 moles of base in the alkaline solution used for the experiment. t' and $1/h'$ are the temperature and the moles of salt per mole of water for which the specific heat, C_p, was interpolated from the deviation plots representing the Bousfield data. In the last column, $-\Delta H$(R) gives the interpolated values for the same concentration and temperature (20°) furnished by the data of Richards and collaborators, as noted. For this interpolation the deviations from linearity of the heat versus $1/h$ were calculated and plotted against the square root of $1/h$; taking the square root removed an excessive bend in the plots. The values of the heat for infinite dilution used were the extrapolated values found in the summary of Richards and Rowe[3] for the formation of potassium chloride, and of Richards and Hall[13] for the formation of sodium chloride. At the time our experiments were concluded the 1929 articles from the Harvard laboratory had not been published and our results for sodium chloride differed from the interpolated values from the older work of Richards and Rowe by about 25 calories, but it will be seen from Table II that our results are in good agreement with the recent values.

In order now to compare our six results at temperatures other than 20°, it is necessary to have temperature coefficients of the heat of neutralization.

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[11] Richards and Gucker, THIS JOURNAL, 51, 712 (1929).

[12] Richards, Mair and Hall, *ibid.*, 51, 727 (1929)

[13] Richards and Hall, *ibid.*, 51, 731 (1929).

The values of Richards and Rowe need corrections, according to the 1929 articles. Using the latest data for sodium hydroxide and hydrochloric acid, and the (R-R) specific heats for sodium chloride given in Table I, new values of the temperature coefficient were calculated from Kirchhoff's law. They lie near a gently sloping line, when plotted against the concentration $(1/h)$, and intercept the axis of zero concentration very close to the value of Noyes, Kato and Sosman.[14] Since, however, ideas have necessarily been used in the interpolation of some of the specific heat data on which the values of the temperature coefficient in the dilute region are based, we see no guarantee that this temperature coefficient curve is substantially correct at low concentrations, and it is not here reproduced. We have used it, however, in an effort to compare our results at various temperatures with the interpolated Harvard values at 20°. From this curve, interpolated values of the temperature coefficient were read off for the necessary concentrations, and our results were corrected to 20° by means of them, assuming, of course, that the coefficient is constant over the whole temperature interval, which cannot be the case from 20 to 50°. The comparison is given in Table III.

TABLE III

ATTEMPTED COMPARISON OF DATA BY THE USE OF TEMPERATURE COEFFICIENTS

Temperature	24.99	32.27	32.27	32.3	50.04	50.04
Dilution (h)	1101	569	566	521	52.9	99.9
Percentage deviation	0.45	0.24	0.71	0.70	0	–1.22

The percentage deviation is the heat of reaction (evolution) calculated from our results minus the corresponding results of Richards and Hall,[13] in percentage of the latter results. Bearing in mind the close agreement shown at 20° in Table II, which was only reached after their recent revision, we do not believe that the disagreement shown in Table III (unless, it may well be, at 50°, in view of the unsatisfactory specific heats at that temperature) is mainly due to experimental error in our heats. Neither does it seem to be principally due to a variation of the temperature coefficient with temperature. The suggestion is strong that the temperature coefficients, extrapolated into the dilute region, cannot be trusted.

Summary

From the measurements of Bousfield and Bousfield, specific heat tables, apparently quite accurate, were deduced for sodium chloride solutions at 20, 25 and 32°, and for potassium chloride solutions at 20 and 25°.

Some data were obtained for the formation by neutralization of sodium and potassium chlorides. The results were computed in the form

$$NaOH\cdot 0.5(h-1)H_2O + HCl\cdot 0.5(h-1)H_2O = NaCl\cdot hH_2O - \Delta H, \text{ at } t^\circ$$

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[14] Noyes, Kato and Sosman, THIS JOURNAL, 32, 159 (1910).

Our experiments at 20° agree very closely for both chlorides with the exact results of Richards and his collaborators for 20°, but when our experiments at other temperatures are compared with them with the aid of temperature coefficients, the agreement is poor. The concentrations at which the discrepancies are significant are rather low, and it appears that the temperature coefficients are not known at sufficiently low concentrations to establish the extrapolated value at zero concentration.

CAMBRIDGE, MASSACHUSETTS

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

DOUBLE SALT FORMATION AMONG THE CARBONATES AND BICARBONATES OF SODIUM AND POTASSIUM

BY ARTHUR E. HILL

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When aqueous solutions of the carbonates and bicarbonates of sodium and potassium are brought to crystallization, five solid phases of the general nature of double salts have been found and identified with certainty. The best known of these is Trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, which has been known for a long period of time and which has been studied from its lower temperature of formation, 21.26°, up to 50° by Hill and Bacon,[1] and more recently up to 89° by Wegscheider and Mehl;[2] at this temperature the latter investigators also believe that two new double salts are formed, for which the evidence is, however, less conclusive than for toe five here under discussion. Known also for a long time, but incorrectly classed as a definite compound in the earlier literature, is the hydrated solid solution $(K_2, Na_2)CO_3 \cdot 6H_2O$, which was shown by Hill and Miller[3] to exist in contact with alkali carbonate solutions over a rather wide range of concentrations, from 34° downward. The anhydrous double carbonate $KNaCO_3$ has been shown[3] to be stable in contact with solution from 25.12' upward to at least 50°, and probably much higher. Recently, in a study of the reciprocal salt pair $K_2CO_3 + 2NaHCO_3 \rightleftarrows Na_2CO_3 + 2KHCO_3$, Hill and S. B. Smith[4] found a new double salt of the formula $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, belonging to the class of double salts without common ion which Meyerhoffer[6] has called tetragene salts. This salt was found only in four-component solutions, and its occurrence and the limits of its field were determined, it was thought, with surety. At the same time that this paper was published, there appeared the valuable and comprehensive work of Teeple upon the

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[1] Hill and Bacon, THIS JOURNAL, 49,2487 (1927).

[2] Wegscheider and Mehl, *Monatsh.*, 49,283 (1928).

[3] Hill and Miller, THIS JOURNAL, 49, 669 (1927).

[4] Hill and Smith, *ibid.*, 51, 1626 (1929).

[5] Meyerhoffer, *Z. anorg. Chem.*, 34, 147 (1902).

Searles Lake deposits; in this there is given[6] a 35° isotherm by de Ropp for the same system, in which our tetragene salt does not appear, but its place is given over to a potassium salt, $K_2CO_3 \cdot 2KHCO_3 \cdot 3H_2O$, which we had not found in our work. and which is the fifth of the double salts which have been claimed for the system. As it was considered necessary to clear up this contradiction, the four-component work has been repeated at the two temperatures in question, 25 and 35°, with the resulting conclusion that both earlier publications contained an error of omission; as will be shown below, both the tetragene salt and the potassium sesquicarbonate (though with a different degree of hydration, as will be shown in the paper following this) occur at both temperatures, with a division of the disputed field between them.

Experimental Methods.—The experiments at the two temperatures have been carried out as in the previous work of Hill and Smith.[4] Pure specimens of the carbonates and bicarbonates of sodium and potassium, in suitable weighed amounts, have been treated with weighed amounts of water and tumbled in a thermostat usually for two days before pipetted samples of the saturated solutions were withdrawn and analyzed. Attainment of saturation with respect to two salts on the lines of isothermally univariant equilibrium, and with respect to three salts at the isothermally invariant points, was proved in every case by the method of adding the components necessary to give the composition of the saturating salts, tumbling the mixture for another day, and again analyzing the solution; where it remained unaltered within the errors of the analysis, equilibrium was assured. For the analysis, one sample of solution was titrated for total alkali with standard hydrochloric acid, using methyl orange as indicator; a second sample was evaporated to constant weight to give total potassium and sodium as carbonate; a third sample was analyzed for total carbon dioxide by adding sulfuric acid and absorbing the evolved gas in soda lime in a Flemming bottle. From these data the composition of the solution was calculated. The samples were weighed from volumetric pipets, from which data densities can be calculated, but not with a high degree of accuracy.

The 25° Isotherm.—The data at 25° are given in Table I and reproduced graphically in Fig. 1. In the table, the abbreviation T. S. is used for the tetragene salt $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, and D.S. for the double salt $K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$.

It will be seen from Fig. 1, which reproduces on a large scale a part of the four-component diagram previously given[4] in full, that the double salt $K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$ found by Teeple at 35° has an existence in this system, but is stable only over a small range of concentrations.

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[6] Teeple, "The Industrial Development of Searles Lake Brines," The Chemical Catalog Co.. Inc., New York, 1929.

Table I

The Data at 25°

Point in Fig. 1	Density	Wright %, satd. soln.				Moles per 1000 moles of H_2O				Solid phases
		K_2CO_3	$KHCO_3$	Na_2CO_3	$NaHCO_3$	K_2CO_3	$(KHCO_3)$	Na_2CO_3	$(NaHCO_3)$	
A	1.559	52.77	0.0	...	..	145.6	...	...	.	K_2CO_3 3/2H_2O
B	1.563	51.23	2.64	...	..	144.8	5.2	...		K_2CO_3·3/2H_2O + D. S.
	1.562	50.77	2.85	...	..	142.8	5.5	...	.	D. S.
	1.554	50.28	3.02	...	..	140.4	5.8	...	. .	D. S.
	1.549	49.77	3.22	...	..	138.0	6.2	...	...	D S.
C	1.545	49.48	3.33	...	..	136.4	6.4	...	..	D S + $KHCO_3$
	1.556	49.90	2.19	...	1.00	138.7	4.2	...	2 3	D. S. + $KHCO_3$
	1.552	50.06	1.26	...	1.85	139.4	2.4	...	4.2	D. S. + $KHCO_3$
Q	1.553	50.05	..	0.38	2.73	139.3	...	1.4	6 3	D S + $KHCO_3$ + T. S.
	1.557	50.55	..	.34	2.52	141.5	...	1.2	5 8	D. S. + T. S.
	1.560	50.91	..	.24	2.44	143.0	...	0.9	5 8	D S + T. S
Z	1.566	51.80	..	.15	2.10	147.0	...	.5	4 9	D. S. + T. S. + K_2CO_3.3/2H_2O
	1.567	51.82	0.44	...	1.79	147.0	0.9	...	4 2	D S. + K_2CO_3·3/2H_2O
	1.565	51.64	1.46	...	0.87	146.0	2.9	...	2 0	D. S. + K_2CO_3·3/2H_2O
B	1.563	51.23	2.64	...	..	144.8	5.2	...		D. S. + KCO_3 3/2H_2O

The 35° Isotherm.—The data at 35° are given in Table II and shown in Fig. 2.

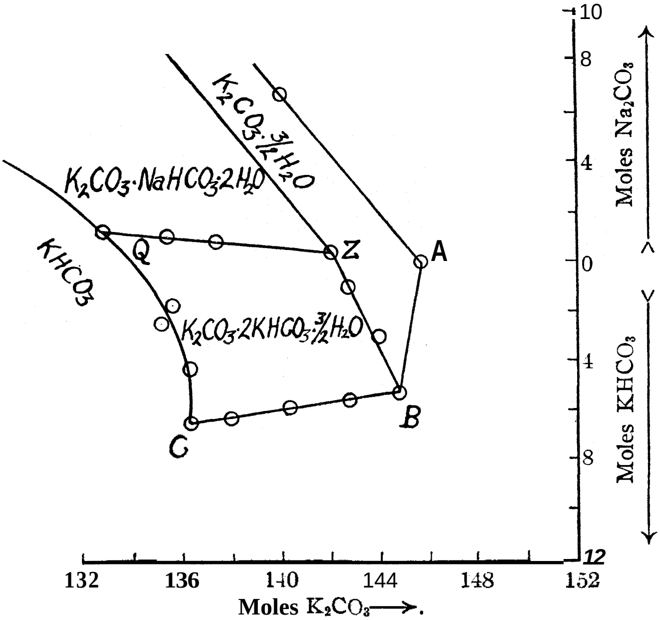

Fig. 1.—System K_2CO_3–$NaHCO_3$–Na_2CO_3–$KHCO_3$–H_2O at 25°.

Comparing Fig. 2 with the comparable part of de Ropp's isotherm at the same temperature, the present work establishes the existence of the isothermally invariant points Q and Z and the existence of separate fields for

TABLE II

THE DATA AT 35°

Point in Fig. 2	Density	Weight %, satd. soln.			Moles per 1000 moles of H_2O					Solid phases
		CO_3	$NaHCO_3$	Na_2CO_3	$KHCO_3$	K_2CO_3	$(NaHCO_3)_2$	Na_2CO_3	$(KHCO_3)_2$	
X	1.571	50.07	..	4.19	..	142.7	...	15.6	...	$K_2CO_3·3/2H_2O$ + $KNaCO_3$
A	1.560	53.56	..	..	..	150.4	...	...	...	$K_2CO_3·3/2H_2O$
B	1.573	51.68	..	..	3.26	149.5	...	...	6.5	$K_2CO_3·3/2H_2O$ + D. S.
	1.563	50.99	..	..	3.48	146.0	...	...	6.9	D.S.
	1.564	50.58	..	..	3.62	144.0	...	...	7.0	D.S.
	1.556	50.00	..	..	3.92	141.5	...	...	7.6	D.S.
C	1.556	49.51	..	..	4.27	139.6	...	...	8.3	D.S. + KHCOa
	1.557	49.96	1.26	..	2.69	141.2	2.9	...	5.2	D.S. + KHCOa
	1.558	50.02	1.93	..	2.01	141.6	4.5	...	3.9	D.S. + KHCOa
	1.557	50.37	2.90	..	0.53	142.1	6.7	...	1.0	D.S. + KHCOa
	1.553	49.81	3.54	0.25	..	139.9	8.2	0.9	...	D.S. + KHCOa
	1.551	49.20	3.49	.64	..	137.4	8.0	2.3	...	D.S. + KHCOa
Q	1.547	48.42	3.58	1.12	..	134.7	8.2	4.1	...	D.S. + KHCOa + T.S.
	1.552	48.52	3.11	1.66	..	135.4	7.1	6.0	...	D.S. + T.S.
	1.562	48.54	2.05	3.10	..	136.7	4.7	11.4	...	D.S. + T.S.
Z	1.568	48.62	1.38	4.25	..	138.6	3.3	15.8	...	D.S. + T.S. + $KNaCO_3$
Y	1.576	50.37	1.19	3.28	..	145.4	2.8	12.4	...	D.S. + $KNaCO_3$ + $K_2CO_3·3/2H_2O$
	1.574	51.20	1.37	2.20	..	147.5	3.2	8.3	...	D.S. + $K_2CO_3·3/2H_2O$
	1.573	51.12	1.75	0.99	..	150.6	4.2	3.7	...	D.S. + $K_2CO_3·3/2H_2O$
	...	52.54	2.17	.17	..	151.8	5.2	0.6	...	D.S. + $K_4CO_3·3/2H_2O$
	1.573	52.57	1.95	..	0.49	152.4	4.6	...	1.0	D.S. + $K_2CO_3·3/2H_2O$
	1.573	52.15	1.17	..	1.82	151.6	2.8	...	3.6	D.S. + $K_2CO_3·3/2H_2O$
B	1.573	51.68	..	..	3.26	149.5	...	...	6.5	D.S. + $K_2CO_3·3/2H_2O$

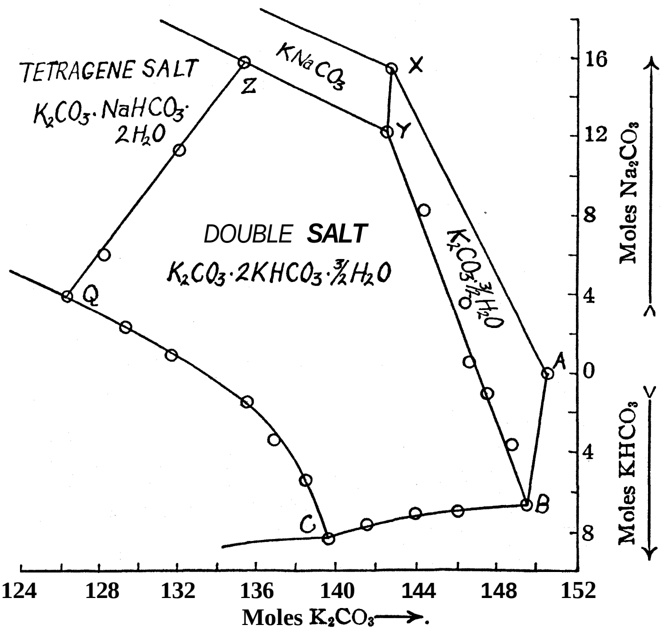

Fig. 2.—System K_2CO_3–$NaHCO_3$–Na_2CO_3–$KHCO_3$–H_2O at 35°.

the double salt and the tetragene salt; this was confirmed by preparing the single salts, each within the concentration range indicated, and subjecting each to an analysis which confirmed its composition beyond doubt. The other points in the diagram were found to be in qualitative agreement with de Ropp's findings, but varying from his by several per cent. in composition. As compared with the 25° isotherm, the figure shows that a rise of temperature increases the range of concentrations within which the double salt can form and decreases the range for the tetragene salt.

Summary

Partial isotherms at 25° and at 35° for the four component system $K_2CO_3 + 2NaHCO_3 \rightleftarrows Na_2CO_3 + 2KHCO_3$ in water have shown that at both temperatures there exist as solid phases the double salt $K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$ and the tetragene salt $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$.

NEW YORK, N. Y.

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

HYDRATED POTASSIUM SESQUICARBONATE, $K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$

BY ARTHUR E. HILL

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The existence of a sesquicarbonate of potassium, intermediate in composition between the normal carbonate and the bicarbonate, has been claimed frequently over a long period of time, and at least as frequently disputed. It appears to have been mentioned first by Berthollet,[1] who obtained it by boiling and cooling a solution of the bicarbonate, and also by cooling a solution of equimolecular proportions of the carbonate and bicarbonate; it is obvious that these operations gave partial decomposition of the bicarbonate into carbonate and that therefore the composition of the solutions was unknown. The only known analyses of the salt were performed by Flückiger,[2] who used an incrustation found upon an earthenware jar containing crude potash, and by Bauer[3] and by Rammelsberg,[4] who prepared their specimen by evaporation and crystallization of a bicarbonate solution; Flückiger assigned to the salt the formula $K_2CO_3 \cdot 2KHCO_3 \cdot 5H_2O$ and Bauer and Rammelsberg gave it the formula $K_2CO_3 \cdot 2KHCO_3 \cdot 3H_2O$; these formulas will be discussed later in this paper. The salt has also been reported more recently by Appleby and Lane,[5] incidental

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[1] Berthollet, *Mem. Arcueil*, 2. 475 (1809).

[2] Flückiger, *Ber.*, 16, 1143 (1883).

[3] Bauer, *Monatsh.*, 4, 341 (1883).

[4] Rammelsberg, *Ber.*, 16, 273 (1883).

[5] Appleby and Lane, *J. Chem. Soc.*, 113, 609 (1918).

to a study of a four-component system, and by de Ropp;[6] in these two publications no analytical data are given, and the formula of Bauer and Rammelsberg is used. A large number of investigators have failed to find this salt upon studying carbonate–bicarbonate solutions, justifying the comment of Mellor,[7] "there is room for doubting the existence of these salts as chemical individuals until the systems have been explored by the aid of the phase rule." Having been among those who failed to find the compound at one time[8] and found it at another,[9] I have thought it well to make a systematic study, to determine the temperature range and concentration range within which the compound has stable existence, and to determine as correctly as possible its true composition.

Experimental Methods.—Solubility measurements have been made for the three-component system K_2CO_3–$KHCO_3$–H_2O at four temperatures. The potassium carbonate, a Kahlbaum preparation which showed as high purity as the sodium carbonate used as the ultimate standard, was first heated over a burner for several hours and then stored in an electric oven at 110°; attempts to dehydrate the sesquihydrate $K_2CO_3 \cdot 3/2H_2O$ at this temperature are likely to be futile, unless very long periods of time are used. The pure bicarbonate was stored over sulfuric acid in an atmosphere of carbon dioxide Weighed amounts of these salts, with weighed amounts of water, were put into 40-cc. glass-stoppered pyrex tubes and revolved in a water thermostat; although twenty-four hours were allowed for the attainment of equilibrium in nearly all cases, it is certain that equilibrium with the liquid is attained in a much shorter time, even when the double salt has to crystallize out as solid phase; an important point, however, is the necessity for adding the carbonate first and insuring that it is well broken up and brought to complete solution before the bicarbonate is added, to prevent the formation of hard lumps of the hydrated carbonate which may remain incompletely changed for long periods. The high heat of hydration of the anhydrous salt makes it easy to bring it completely into solution. After attainment of equilibrium, two 5-cc. samples were withdrawn from each tube; one was titrated for total alkali by hydrochloric acid solution, using methyl orange as indicator, and the second was treated with sulfuric acid in a suitable train and the carbon dioxide absorbed by soda lime in a Flemming bottle. Tests showed that these two determinations were accurate to within 0.1%; the calculation of the carbonate–bicarbonate ratio from them includes a multiplication which would make errors in the total composition of the order of 0.5%, but the smoothness of the curves obtained

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[6] De Ropp, see Teeple, "Industrial Development of Searles Lake Brines." The Chemical Catalog Co., Inc., New York, 1929, p. 132.

[7] Mellor, "Comprehensive Treatise," Vol. II, London, 1922, p 779.

[8] Hill and Hill, THIS JOURNAL, 49, 967 (1927).

[9] See previous paper, Hill, *ibid.*, 52, 3813 (1930).

indicates that the actual errors were much less. The weights of solution delivered by the volumetric pipets gave rough figures for the densities of the solutions.

The Isotherms,-—The solubility measurements, which were carried out at four temperatures, from 5 to 50°, are given in the following table Columns 5 and 6 give the composition of the mixture weighed into the tubes; Cols. 3 and 4 give the composition of the saturated solutions. The

TABLE I

TERNARY SYSTEM, K_2CO_3–$KHCO_3$–H_2O

Point in Fig 1	Satd. solution Density	K_2CO_3	$KHCO_3$	Orig. complex K_2CO_3	$KHCO_3$	Solid phases
	5° Isotherm					
A	1.543	51.53	..	55.0	0.0	$K_2CO_3\cdot 3/2H_2O$
n	1.155	50.59	1.72	..	..	$K_2CO_3\cdot 3/2H_2O$ + D. S.
	...	50.03	1.77	49.2	6.0	D. S.
	1.543	49.91	1.90	49.0	6.0	D. S.
C	1.542	49.65	1.96	...	..	D. S. + $KHCO_3$
	1.509	46.38	2.55	44.0	8.0	$KHCO_3$
D	1.137	...	20.15	...	30.0	$KHCO_3$
	25" Isotherm					
A	1.559	52.77	..	57.0	..	$K_2CO_3\cdot 3/2H_2O$
B	1.563	51.23	2.64	...	..	$K_2CO_3\cdot 3/2H_2O$ + D. S.
	1.562	50.77	2.85	49.16	7.99	D. S.
	1.554	50.28	3.02	48.95	8.03	D. S.
	1.549	49.77	3.22	48.48	7.92	D.S.
C	1.545	49.48	3.33	...	..	D. S. + $KHCO_3$
	1.538	48.14	3.56	46.41	7.03	$KHCO_3$
	1.526	47.20	3.51	45.04	7.98	$KHCO_3$
	1.484	43.89	4.41	38.00	17.00	$KHCO_3$
	1.485	42.82	4.67	41.63	7.41	$KHCO_3$
	1.402	34.71	7.35	30.00	20.00	$KHCO_3$
	1.316	23.36	12.19	20.00	25.00	$KHCO_3$
	1.272	16.98	15.45	15.00	25.00	$KHCO_3$
	1.228	10.00	19.31	9.00	28.00	$KHCO_3$
D	1.187	0.00	26.78	...	..	$KHCO_3$
	35° Isotherm					
A	1.560	53.56	0.0	56.0	54.0	$K_2CO_3\cdot 3/2H_2O$
B	1.573	51.68	3.28	...	..	$K_2CO_3\cdot 3/2H_2O$ + D. S.
	1.563	50.99	3.48	49.96	7.00	D. S.
	1.564	50.58	3.62	50.00	7.00	D. S.
	1.556	50.00	3.92	48.52	9.00	D. S.
C	1.656	49.51	4.27	48.08	7.99	D. S. + $KHCO_3$
	1.548	48.93	4.27	46.96	8.00	$KHCO_3$
	1.441	37.73	7.50	34.97	13.99	$KHCO_3$
	1.329	23.04	14.21	20.00	24.98	$KHCO_3$
	1.252	10.04	22.10	8.98	29.99	$KHCO_3$
	1.208	0.97	28.82	...	..	$KHCO_3$
	1.200	0.00	29.60	...	..	$KHCO_3$

Table I (*Concluded*)

Point in Fig. 1	Satd. solution			Orig. complex		Solid phases
	Density	K_2CO_3	$KHCO_3$	K_2CO_3	$KHCO_3$	
			50° Isotherm			
A	...	54.8	0.0	. .		$K_2CO_3 \cdot 3/2H_2O$
B	1.584	52.85	3.83	...	..	$K_2CO_3 \cdot 3/2H_2O$ + D. S.
	1.581	51.97	4.40	...	..	D S.
	1.569	50.92	4.97	50.01	7.01	D. S.
C	1.565	49.65	5.77	...	..	D. S. + $KHCO_3$
D	...	0.0	34.2	...	..	$KHCO_3$ (Dibbetts)

abbreviation D. S. is used for the double salt as solid phase, $K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$.

At each of these four temperatures, there is clear proof of the existence of three solubility curves, one each for $K_2CO_3 \cdot 3/2H_2O$, for $KHCO_3$, and for the double salt; the isothermal invariance of the points marked B and C was established by analyses of two or three solutions in each case, made up from varying ratios of the three components. The solubility curve for the compound is very short, covering only a concentration range of 1 to 2%, as shown by the curve BC in Fig 1, the isotherm for 25°; the narrow limits of this concentration give the explanation as to why the salt has been overlooked on so many occasions. Figure 2 has been drawn so as to show these solubility curves on a much larger scale, from which it appears that the range of stable existence for the double salt, always narrow, becomes more and more restricted as the temperature falls; a rough graphic extrapolation of the curves drawn through the B and C values indicates that the

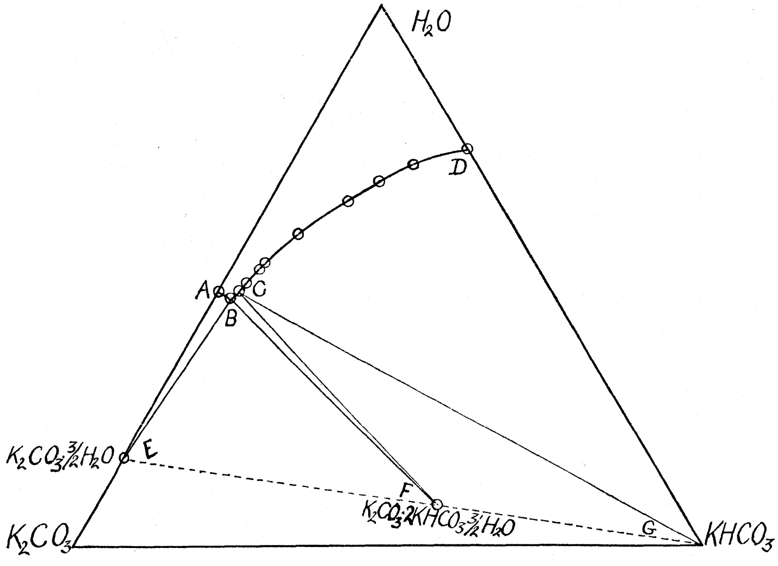

Fig. 1.—25° Isotherm for system K_2CO_3–$KHCO_3$–H_2O.

salt must cease to have stable existence at some temperature not greatly below 5°. It was possible, however, to draw some *a priori* conclusions as to this lower ternary transition temperature of the salt, by means of thermochemical considerations. Since the salt exists only above this temperature, it follows by application of the van't Hoff law of mobile equilibrium that the phase reaction by which it is formed from solution and the solid salts adjacent to it in the diagram must be an endothermal reaction. If it were formed from the bicarbonate and the sesquihydrate $K_2CO_3{\cdot}3/2H_2O$, its formation would in all probability be exothermal, since the reaction would be a simple additive reaction of the two salts. In order to have the reaction endothermal, the compound would have to be formed from compounds of a higher degree of hydration; of such compounds, only one is known, the hexahydrate $K_2CO_3{\cdot}6H_2O$, which Hill and Miller[10] have shown to exist only below −6.2°; it may be concluded, therefore, that the ternary transition temperature of the compound is below −6.2°, and that the phase reaction is

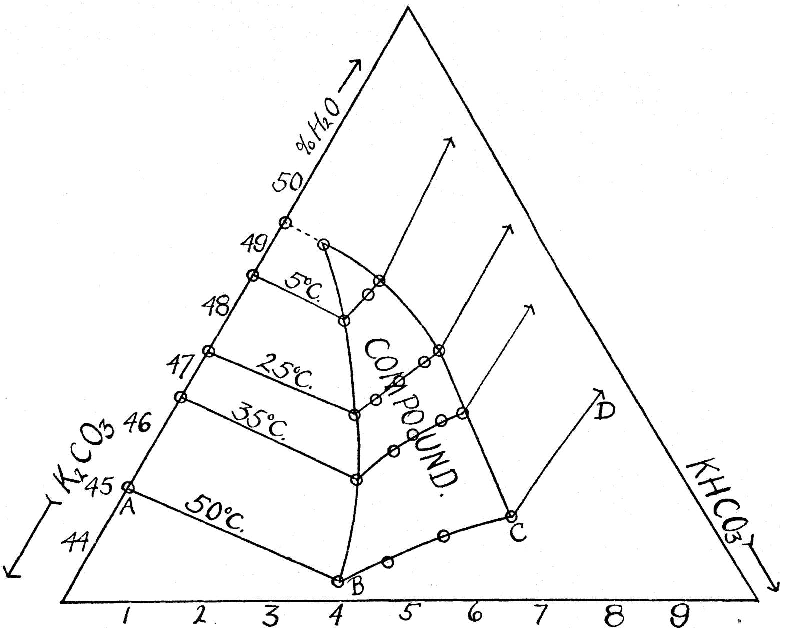

Fig. 2.—System K_2CO_3–$KHCO_3$–H_2O; partial isotherms.

$$K_2CO_3{\cdot}6H_2O + 2KHCO_3 \rightleftharpoons K_2CO_3{\cdot}2KHCO_3{\cdot}3/2H_2O + \text{Solution} - x\ \text{cal.}$$

Experimental confirmation of this reasoning was had by means of cooling curves of complexes made up to fall within the proper range at low temperatures; they were first cooled to about −8° and seeded with the compound

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[10] Hill and Miller, This Journal, 49, 669 (1927).

$K_2CO_3 \cdot 6H_2O$ which can be secured only by undercooling potassium carbonate solution to below $-20°$.[10] The temperature then rose nearly to $-6.2°$, indicating that the transition temperature of hydrated potassium carbonate is but slightly affected by the small amount of bicarbonate in the solution. On being subjected to the temperature of an ice–salt bath, the solution could be undercooled a few tenths of a degree but showed a long continued halt at $-9.2°$, this being taken as the decomposition temperature of the compound. Efforts to secure a halt in the warming curve were all fruitless, indicating that the formation of the compound is not a rapid reaction. Inasmuch as the ternary transition temperature could not be confirmed on rise of temperature the best approximation is the temperature $-9.2°$, which is the highest temperature obtained on the cooling curve.

Composition of the Compound.—Early in the work it became apparent that the compound could not possibly have the composition assigned to it by Fluckiger or by Bauer and Rammelsberg; the tie lines in the area for the compound showed at each temperature a much steeper inclination toward the base line of Fig. 1 than could be made to pass through the alleged composition of the salt. This indicated that the compound must contain either more potassium carbonate than assigned to it previously or less water; a decision could not be arrived at through this means alone, for the extrapolation of lines so nearly parallel as are the tie lines in this narrow area would require an accuracy of analysis which is not attainable. Inspection of the original analytical data of the three authors mentioned showed that their agreement with the proposed formulas was really a fictitious one; arranged by them in terms of percentage of K_2O and CO_2 found, the agreement with the formulas did not look bad, but when recalculated to the ratio of K_2CO_3 to $KHCO_3$ the disagreement is startling. The results of the calculation are given in Table II, together with the critical analysis discussed later in this paper.

TABLE II

COMPOSITION OF DOUBLE SALT

		Ratio $\frac{\text{Moles } K_2CO_3}{\text{Moles } KHCO_3}$	Proposed formula
Rammelsberg	1883	1.00:2.57	$K_2CO_3 \cdot 2KHCO_3 \cdot 3H_2O$
Bauer	1883	1.00:2.27	$K_2CO_3 \cdot 2KHCO_3 \cdot 3H_2O$
Flückiger	1883	1.00:2.08	$K_2CO_3 \cdot 2KHCO_3 \cdot 5H_2O$
Hill	1930	1.00:1.94	$K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$

Examination of these figures makes it problematical why Rammelsberg should assign the formula for a 1:2 ratio when the ratio found is less than 2:5. The results of Bauer and Fluckiger, while nearer to the 1:2 ratio, are still distinctly high, and the water content given is very much higher in all three cases than I have found it to be. The explanation is not hard to give for all three cases; the solids used for analysis in every instance must have contained as impurity solid $KHCO_3$ and solution, the latter tending to give a high value for water and (by its high K_2CO_3 content) tending also to give a high figure for K_2CO_3 and thus to counteract the effect of the first impurity. Since the ratios are nevertheless high in $KHCO_3$ content, the samples must have contained very large amounts of solid $KHCO_3$.

Although the necessary conditions for obtaining a pure specimen of a salt showing incongruent solubility follow quite directly from phase-rule considerations, these conditions do not appear to have been stated often and have been observed still less often. A brief discussion of them is not out of place. The first necessary condition is that the compound be isolated after a complete phase-rule study at the temperature decided upon, to insure that it has been precipitated as the one solid phase in equilibrium with its saturated solution and not as one of the two phases precipitated from isothermally invariant mixtures, such as those covering the large areas BEF and GCF of Fig. 1. Second, comes the trying question of the mother liquor, which in all cases of incongruent solubility is different in composition from the salt and in this case is very widely different. Recrystallization from water is, of course, out of the question, since water brings about the decomposition of an incongruently soluble salt. Removal of as much mother liquor as possible, by mechanical means such as centrifuging, is highly desirable; but the essential point is that, inasmuch as mother liquor is necessarily present, its amount shall be definitely known, so that a correction of the final analysis may be made. The practice of allowing the moist crystals to undergo air-drying before analysis is entirely useless, except in so far as it reduces the water content to a closer approximation to the truth; the salt is then contaminated by the residuum from the evaporated mother liquor, the amount of that contamination being entirely unknown and not capable of being allowed for in the calculation. To determine the amount of such mother liquor, the well-separated crystals may be placed in a desiccator over the next lower hydrate and brought to constant weight; the loss of water corresponds to a definite precipitation of salts, known in amount and character from the analysis of the solution, which quantities may then be introduced into the subsequent analysis as a perfectly definite and reliable correction. Such a procedure will give material which may be analyzed with confidence as to its composition in respect to salts and also as to water of crystallization.

Preliminary examination by this method showed that the double salt of this discussion contained K_2CO_3 and $KHCO_3$ in ratio close to 1.00 to 2.00, and that the water content is between 7 and 8%. The water of crystallization, as reported by Rammelsberg, Bauer and Flückiger, is of the order of 15 to 20%, showing the presence of a very large amount of mother liquor in the moist crystals; such large amounts are inevitable if simple filtration is used with so highly concentrated a solution as exists in this case. The clear deduction as to these three analyses is that those investigators analyzed very wet samples, and therefore found the apparent water of hydration much too high. This large amount of mother liquor would give the crystals a large excess of K_2CO_3 over the true ratio; to account for the fact that the analyses show, on the contrary, too much $KHCO_3$, we must believe that the systems, at the time the samples were taken, were represented by complexes within the isothermally invariant triangle FCG and that the solid was, therefore, a mixture of the double salt with excess $KHCO_3$. This accords wholly with Rammelsberg's and Bauer's method of preparation by partial decomposition of a solution saturated with $KHCO_3$.

For a final analysis, a large sample of double salt was prepared from a solution analyzing as containing 49.96% K_2CO_3, 1.93% $KHCO_3$ and 48.11% H_2O, falling on the solubility curve for the double salt at 5°. The sample was centrifuged for two minutes at 4000 r. p. m., and brought to constant weight over double salt partially dehydrated by sulfuric acid. The water lost as water of solution for two samples was, respectively, 2.7 and 5.65% of the wet solid. Table III gives the results for the two samples.

TABLE III

ANALYSIS OF DOUBLE SALT

	Analysis of dried sample, %	Corrected, %	Molar ratio	2d correction, %	Molar ratio	% Calcd. for $K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$
Sample 1						
K_2CO_3	40.45	38.60	1.00	38.47	1.00	37.82
$KHCO_3$	51.21	53.41	1.91	54.13	1.94	54.78
H_2O	8.34	7.99	1.59	7.40	1.48	7.40
Sample 2						
K_2CO_3	42.21	38.99	1.00	38.60	1.00	37.82
$KHCO_3$	46.78	52.28	1.85	54.00	1.93	54.78
H_2O	11.01	8.73	1.71	7.40	1.47	7.40

In Col. 2 are given the results of the analyses of the samples as brought to constant weight. Column 3 gives the results corrected for the loss of 2.7 and 5.65% of water of solution from the wet samples. These corrected results show, by the molar ratio of Col. 4, that the two salts approximate a 1:2 ratio, and that the water of hydration is distinctly less than two moles. From this it may be assumed that the water of hydration is probably 1.5 moles, corresponding to that of the sesqui-hydrated potassium carbonate. On that basis a further correction may be made, namely, that the slight excess of water found (0.59 and 1.33%) represents mother liquor enclosed by the process of drying, and not given up during the drying periods, which were ten and thirty days, respectively. We can then determine algebraically the excess solution still present and correct for its presence, as in the former case. Correcting so as to bring the water content down to the assumed value of 7.40%, we have the figures of Col. 5 and the molar ratio of Col. 6, which agree with the calculated values as closely as may be expected. The formula of the salt is thereby established as $K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$, an addition compound of $K_2CO_3 \cdot 3/2H_2O$ and $KHCO_3$ without change in hydration.

Summary

1. Isotherms have been constructed for the ternary system K_2CO_3–$KHCO_3$–H_2O at 5, 25, 35 and 50°.

2. The double salt first observed by Berthollet has been found to have a stable existence in contact with solution from $-9.2°$, its lower transition temperature, to something above 50°, but always within a very narrow range of concentrations.

3. A critique is offered of the methods for preparing incongruently soluble double salts for analysis.

4. The formula of the double salt is found to be $K_2CO_3 \cdot 2KHCO_3 \cdot 3/2H_2O$.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

THE QUENCHING OF MERCURY RESONANCE RADIATION. I. THE SATURATED HYDROCARBONS

BY JOHN R. BATES

RECEIVED JUNE 6, 1930 PUBLISHED OCTOBER 6, 1930

The reactions of the saturated hydrocarbons under the influence of excited mercury atoms have been studied by Taylor and Hill,[1] who found that, with the exception of methane, they are all decomposed to give hydrogen, methane and high-boiling mixtures such as are obtained in the thermal "cracking" of hydrocarbons. This behavior, which is analogous to that observed in the presence of hydrogen atoms,[2] seemed worthy of further study to determine whether the inactivity of methane arose from its inability to receive the energy of the mercury atom or whether it was similar to the case of hydrogen and excited cadmium atoms,[3] where the energy is transferred, but no reaction results.

Measurements have therefore been made of the quenching of mercury resonance radiation by the four hydrocarbons—methane, ethane, propane and butane—which make quite clear the reasons for the results obtained by Taylor and Hill and also furnish values for the collision radii for collisions of the second kind between excited mercury atoms and the hydro-

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[1] Taylor and Hill, THIS JOURNAL, 51, 2922 (1929).

[2] Bonhoeffer and Harteck, *Z. physik. Chem.*, 139, 64 (1928).

[3] Bates, *Proc. Nat. Acad. Sci.*, 14, 849 (1928).

carbons, which are becoming of interest in the light of recent theoretical considerations of such collisions.

Experimental

The method used is that due to Zemansky.[4] A source of mercury resonance light (L in Fig. 1) is focused on one quartz window of a resonance lamp T, which consists of a tube containing mercury vapor at a definite pressure. The resonance light excited is then taken out of the quartz window perpendicular to the first and collimated by a lens. This parallel light is passed through a cell (B) of 8 mm. thickness and 40 mm. diameter, immediately behind which is an iris diaphragm. Behind this is a quartz platinum hydrogen filled photo-electric cell which can be moved so that it is either in contact with the diaphragm (position R) or at a distance of 15 cm. The photo-electric current is measured by a Compton quadrant electrometer.

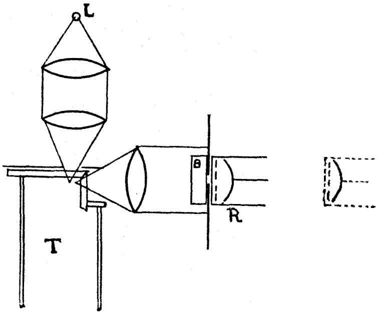

Fig. 1.

In measuring the quenching a reading is taken with B containing mercury vapor at 20°, and the photo-electric cell at R. The cell is then moved back to a position which records only the parallel light passing through the diaphragm. The difference between these two readings $I_{\mathrm{R}} - \mathrm{I}$, is the resonance light emitted by B. With the photo-cell at R, readings are then taken at various pressures of the foreign gas whose quenching is to be determined. The percentage of resonance light emitted, J, is then calculated from the equation

$$J = \frac{(I_{\mathrm{R_p}} - I_{\infty_\mathrm{v}})}{(I_{\mathrm{R_v}} - I_{\infty_\mathrm{v}})} \times 100$$

As a source of light a mercury arc rich in resonance light, which has already been described,[5] was used.

In order to have a standard by means of which fluctuations of the intensity of resonance light emitted by the resonance lamp could be corrected for, the cell B was made movable and could be replaced by a fused quartz window covered with a film of gelatin. Immediately before and after each reading of the resonance light a reading of the light transmitted by this "standard" was made.

To have as monochromatic resonance light as possible the precautions described by Kunze[6] were taken in constructing the resonance lamp.

Preparation of the Gases.—The hydrocarbons were obtained from cylinders containing these gases, whose source was natural gas. It was thought these would be considerably freer from hydrogen than any laboratory source. Since hydrogen is known to quench mercury resonance radiation at pressures of the order of 0.01 mm., it was important to insure its absence.

Methane, propane and butane were taken from the tank, dried over phosphorus pentoxide, frozen out and redistilled twice *in vacuo*, the middle fraction being taken both times.

Ethane, which contained 10–15% ethylene as it came from the tank, was twice bubbled through saturated bromine water and carried a distance of approximately

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[4] Zemansky, *Phys. Rev.*, 36,919 (1930).

[5] Taylor, THIS JOURNAL, 48, 2840 (1926); Bates and Taylor, *ibid.*, 49, 2483 (1027).

[6] Kunze, Ann. *Physik*, 85, 1013 (1928).

three meters saturated with bromine vapor, then through sodium hydroxide solution, soda lime and phosphorus pentoxide. Higher-boiling substances such as bromine and bromides were removed by a solid carbon dioxide–ether mixture. It was then subjected to the distillations as in the other cases.

The intensity of the light falling upon the cell from the resonance lamp is very small and quite insufficient to bring about enough decomposition of the hydrocarbons into hydrogen to affect the values observed. Furthermore, this was experimentally shown by the following method. The gas was admitted in successive small quantities, a reading being taken after each addition. This process takes about six hours, allowing sufficient time to reestablish the equilibrium vapor pressure of mercury. disturbed by the flow of gas into the cell. The gas was then pumped out in successive quantities, readings were again taken and found to agree within the experimental error with those observed previously.

Experimental Results

The quenching curves for the hydrocarbons are given in Figs. 2 and 3. They are represented by plotting J, the percentage of resonance light emitted, against the pressure of the various gases.

In determining the efficiencies of collisions between excited mercury atoms and foreign gas molecules, it has been the custom to take the value of the pressure where J equaled 50% and, assuming this to be the pressure at which the mercury atom has an equal chance of emitting or losing its energy on collision, calculate the number of fruitful collisions.[7] However, Zemansky[8] has derived a more exact relationship where τk = f (J,p,α,d); τ being the mean life of an excited mercury atom in the 2^3P_1 state (10–7 sec.), k the number of second kind collisions per atom per second, p the vapor pressure of mercury in the cell, a the absorption coefficient of mercury under the conditions employed, and d the thickness of the cell. From τk the value σ_E, or collision distance between excited mercury atoms and foreign gases, can be obtained from the gas kinetic equation

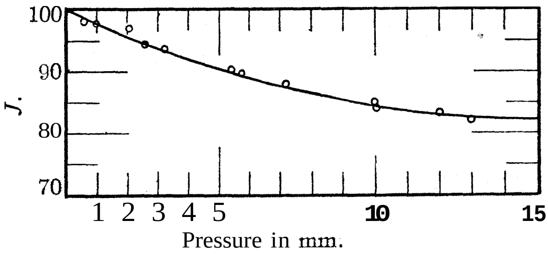

Fig. 2.—Methane.

$$K = 2\sigma_E^2 \times 9.81 \times 10^{18}\frac{p}{T}\sqrt{2\pi kT\left(\frac{1}{M}+\frac{1}{m}\right)} \tag{1}$$

Substituting for T = 293.0°, and multiplying through by τ

$$\sigma_E^2 = \frac{\left(\frac{\tau K}{p}\right)}{3355\sqrt{\frac{1}{M}+\frac{1}{m}}} \tag{2}$$

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[7] Stuart, *Z. Physik*, **32, 262** (1925).

[8] Zemansky, Phys. Rev., 31, **812** (1928).

Since the relationship between τk and J involves a laborious calculation involving the absorption coefficient of mercury, which could not be accurately determined by the system as set up, a curve representing this dependence was obtained from a curve of τk against p obtained through the kindness of Dr. Zemansky, who measured propane taken from the same sample as that used in the present measurements. From this and the propane curve in Fig. 3, the curve in Fig. 4 was obtained. Then from a knowledge of J:p and τk:J (Figs. 3 and 4) the final results in Fig. 5, which give the number of collisions of the second kind per excited mercury atom at any given foreign gas pressure, were obtained. The relationships for the various hydrocarbons are remarkably linear with respect to pressure, which is as expected. The slope of these curves gives $\tau K/p$ which, when placed in the numerator of Equation 2, gives values for σ_E.

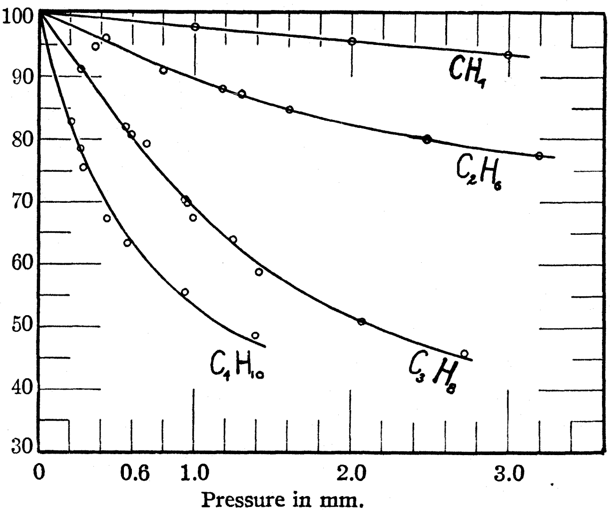

Fig. 3.

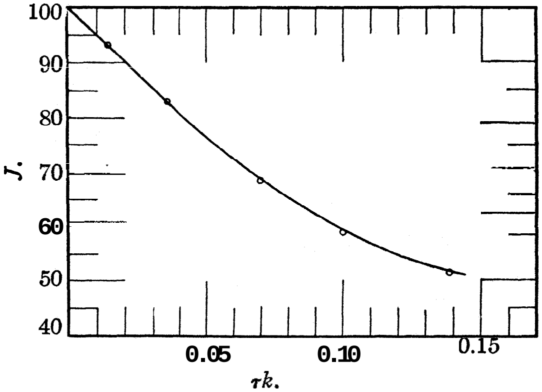

Fig. 4.

In Table I are shown the values of $\tau k/p$, and σ_E^2 thus obtained, together with σ_N^2 from kinetic theory. The values are accurate to within 5% and within themselves agree probably to a much better value.

TABLE I

RESULTS

Gas	$\tau K/p$	$\sigma_{\mathcal{E}}^2 \times 10^{16}$	$\sigma_N^2 \times 10^{16}$[a]
CH_4	0.004	0.059	11.6
C_2H_6	.021	.421	16.4
C_3H_8	.0695	1.60	≥17?
C_4H_{10}	.158	4.06	≥18?
H_2[b]	1.13	6.01	8.89

[a] Herzfeld, "Handbuch der Physik," Vol. 22, p. 409.

[b] Taken from Zemansky for comparison.

From the $\tau k/p$ values it can be seen immediately that the relative probability of a transfer of the energy of the mercury atom does decrease as we go from butane down to methane, reaching a very small value for the latter. However, this does not indicate that methane should he entirely unaffected, especially at high pressure, if the energy is given over at all. There is always the possibility that the mercury atom only gives up the 0.2 volt which separates the 2^3P_1 state from the metastable 2^3P_0 level, which process is known to occur in many cases, e. g., helium, carbon monoxide, nitrogen, water, etc. In this case the energy transferred, being too small to bring about any chemical reaction, would be accommodated in the translational and vibrational degrees of freedom of the methane molecule, and at low pressures the metastable mercury atom, having a long life, would diffuse to the walls and give up the remaining energy. At higher pressures, where the metastable atoms make a large number of collisions in diffusing to the walls, there is a probability that in some collision there will be sufficient kinetic energy available to bring the mer-

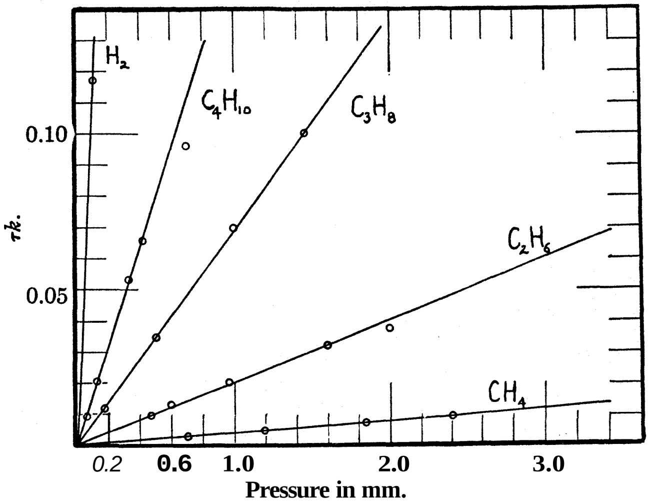

Fig. 5.

cury atom back to the 2^3P_1 level, where it may either radiate or be quenched once more.[9] The effect of this would obviously be to lower the apparent quenching at high pressures,

In order to see whether this occurred, the measurements on methane were extended to pressures of 200 mm. The results are plotted in Curve I of Fig. 6. The value of J at first decreases and then increases to impossibly high values, due to decreased absorption of mercury vapor in the presence of methane at higher pressures. The latter was determined by measurement and shown in Fig. 7, expressed as percentage transmission with transmission in *vacuo* 100%.[10] It will be seen that this change

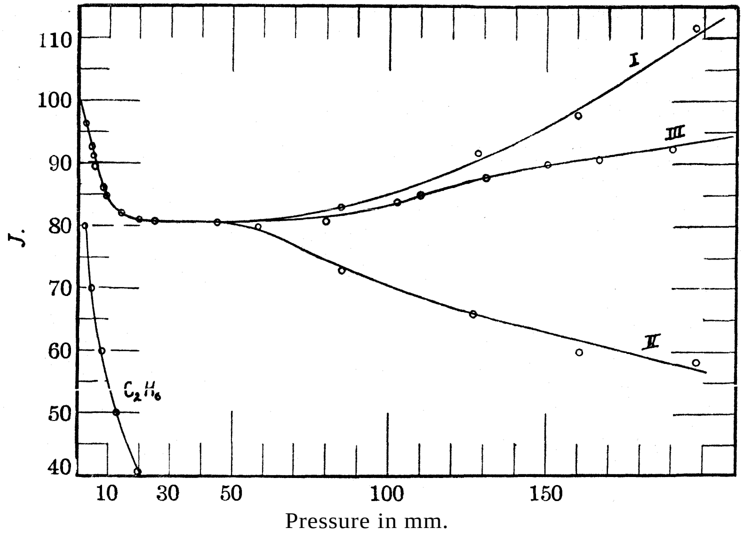

Fig. 6.

in absorption will not affect the results in Fig. 2, since at the pressures there considered, there is no measurable difference from vacuum conditions. However, at high pressures the equation $J = (I_{R_p} - I_{\infty v})/(I_{R_v} - I_{\infty v})$ must now have $I_{\infty p}$, instead of $I_{\infty v}$ in the numerator. This correction, applied to Curve I in Fig. 6, gives Curve II. An additional correction to this, due to the fact that, with lower absorption, there is naturally proportionately lower emission of resonance light, gives as the final result III for the corrected quenching curve of methane at high pressures, obtained by multiplying the values of II by the corresponding values

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[9] See Foote, Phys. *Rev.*, 30,288 (1927), and many other papers.

[10] The shape of the curve is very readily understood when it is realized that the line emitted even by a resonance lamp is somewhat broader than the Doppler breadth of mercury absorption in *vacuo*. Hence when the absorption line is at first broadened absorption increases, until the breadths coincide, after which there is a decrease. See Zemansky, Orthmann, and others for a quantitative treatment of this effect.

of transmission as obtained from Fig. 7. While this is perhaps not exact, due to the necessary assumptions, it is a very close approximation, and is what would be expected for a gas which quenched by lowering the mercury atoms to the metastable level. These atoms are able to diffuse to the walls and give up their energy to a pressure of about 10 mm., where an appreciable number begin to be returned to the 2^3P_1 level. This is also an indication that the methane used was surprisingly free from hydrogen, since metastable mercury atoms are efficiently quenched by this gas.[11] The values for ethane are shown up to 20 mm. (the curve continued for somewhat higher pressures) to show that there is no break similar to that in methane. This does not necessarily mean that ethane does not bring some atoms to the metastable level, but, that if it does bring any considerable number, the transfer between these atoms and the ethane molecule is extremely efficient. Water, for instance, is known to bring about both types of transfer.[12]

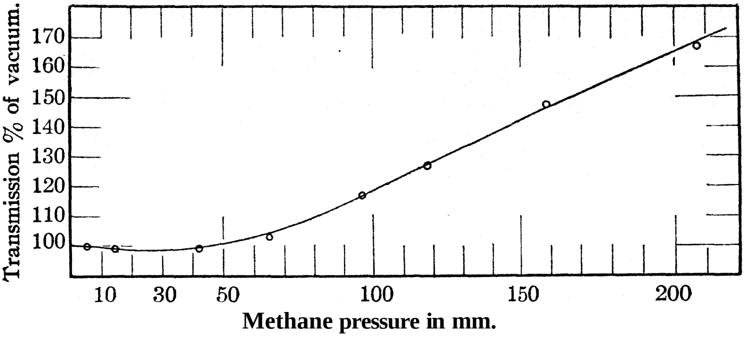

Fig. 7.

Discussion of Results

The fact that methane quenches mercury resonance radiation in the same manner as the more inert type of gas molecules is quite in agreement with the other properties of the methane molecule.[13]

It is interesting to compare the pressure at which the methane quenching curve undergoes a break (about 10 mm.) with the value of the minimum in Zemansky's[8] determination of β, the exponential in the expression for the lifetime of an excited mercury atom in the presence of nitrogen, which is at 8 mm. These should roughly correspond, since the minimum in the β-curve is also due to the presence of a large number of metastable atoms, which are prevented from diffusing to the walls.

A calculation of the number of collisions made by a mercury atom in

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[11] Meyer, *Z. Physik*, 37, 639 (1926).

[12] Gaviola, *Phil. Mag.*, 6, 1191 (1928).

[13] Glockler, THIS JOURNAL, 48, 2021 (1926).

diffusing a distance of 1.5 mm. (the average distance traveled in a layer 3 mm. thick, where, in the side of the cell nearest the source of light, about 50% of the excited atoms are formed) using the Einstein displacement equation

$$AX^2 = 2Dt$$

where t is the time in seconds and D the diffusion coefficient, obtained from the value for that of mercury into nitrogen (the values of diffusion coefficients into methane and nitrogen are, as a rule, very close in value) in the "International Critical Tables," and the value of K, the number of collisions per second per atom, gives a value of 7×10^4. The number of collisions made in which one has sufficient energy available to raise a metastable atom to the 2^3P_1 state is about 2.5×10^3, making every atom, in diffusing this distance, suffer about 28 collisions in which it might be raised to the higher level.

These results explain very satisfactorily why methane does not react as do the other hydrocarbons, since it cannot obtain sufficient energy from the excited mercury atoms,

The mechanism of the reactions of the higher hydrocarbons is in all probability quite complicated. In all cases, as soon as some hydrogen is formed, the reactions go in two ways—by the direct action of the excited mercury atoms on the hydrocarbons, and also by the reaction of hydrogen atoms produced by collisions with hydrogen molecules. From the ratios of the $\tau\bar{K}/p$ values in Table I we can see that with ethane there is an equal probability of hydrogen atom or hydrocarbon decomposition, when hydrogen is present to the extent of 2%, with propane at 6%, and butane at 15%. Thus, in those reactions of Taylor and Hill where hydrogen predominated, the majority of the action came through the agency of hydrogen atoms.

Thanks are due Dr. M. Zemansky for much helpful advice and discussion during the course of this work.

Summary

The quenching of mercury resonance radiation by the gases methane, ethane, propane and butane has been measured, and values for the effective collision cross section have been calculated. Methane has been shown to quench to the metastable level. The results are in agreement with the mercury photosensitized decompositions of these hydrocarbons.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ST. LOUIS UNIVERSITY]

AN X-RAY STUDY OF THE CONSTITUTION OF SOME COPPER–NICKEL–ALUMINUM–MANGANESE ALLOYS[1]

BY LYMAN J. WOOD

RECEIVED JUNE 9, 1930 PUBLISHED OCTOBER 6, 1930

Previous work[1a] has shown that certain copper–nickel–aluminum–manganese alloys composed of 1% Mn, 2–6% Al and having a nickel–copper ratio of 1.5–2.5 possess some very valuable properties. Some of these alloys will effectively resist corrosion by strong nitric acid for long periods of time, have tensile strengths of from 60,000 to 100,000 pounds per square inch and can be machined very easily. The manganese appears to have a very important influence on the tensile strength, the alloys containing 1% of manganese having approximately double the tensile strength of those without it.

A comparison has also been made between the properties of these alloys when chill-cast, sand-cast and annealed and the equilibrium diagram studied by means of cooling curves, photomicrographs and density changes.[2] It has been shown that these alloys are for the most part composed of one kind of solid solution but a second constituent was indicated which could not be positively identified by means of photomicrographs. In view of this fact an x-ray study has been made of the part of the system copper–nickel–aluminum–manganese having the composition indicated above.

Methods and Apparatus.—The apparatus was constructed according to suggestions of Wyckoff[3] and Bain.[4] The sample was reduced to a 200-mesh powder and rotated at the center of an arc of approximately 10 cm. radius inside of which the x-ray film was placed. The film holder was arranged so that the first few lines of the pattern were obtained on each side of the zero. The film holder was standardized by using sodium chloride as a standard, the salt being mixed with the sample in order to avoid errors due to differences in densities. The tube, which had a molybdenum target, was operated continuously at 35 kv. and 10 ma. and the x-rays were filtered through zirconia. The rays used were the MoKα doublet.

Table I shows data for check runs for salt and for one of the alloys where L stands for the film distances in millimeters from the zero beam to the

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[1] Read before the physical and inorganic section of the Atlanta Meeting of the American Chemical Society.

[1a] L. J. Wood and S. W. Parr, Preprint of the American Institute of Chemical Engineers, December 2, 1925.

[2] L J Wood, *J. Phys. Chem.*, 31, 1693–1703 (1927).

[3] Wyckoff, "The Structure of Crystals," The Chemical Catalog *Co.*, New York, 1924.

[4] Bain, *Chem. Met.*, 25, 657–663 (1921).

middle of the lines indicated.[5] By taking 5.628 Å. for the cube edge of sodium chloride and 0.710 Å. for the average wave length of the MoKα doublet and substituting into the formula $n\lambda = 2d$ sin 8 and setting 8 proportional to L, we get $\Theta = 0.2949L$ for this particular film holder when using the MoKα doublet.

TABLE I

COMPARISON OF DATA FROM DUPLICATE RUNS

Equations: L = Distance from zero to middle of line in mm.

Material	Indices (*hkl*)	L 1st run	L 2d run	L Av.
	200	24.55	24.6	24.58
	220	34.95	34.8	34.88
Rock salt	222	42.75	42 8	42.78
	400	49.75	49.6	49.68
	420	55.55	55 7	55.63
Alloy 104	111	34.15	34.21	34.18

TABLE 11

COMPARISON OP OBSERVED DATA FOR ROCK SALT WITH CALCULATED VALUES

Equations. $X(h^2 + k^2 + l^2)^{1/2}/2a = \text{Sin}\,\Theta$; $6 = 0.2949L$

Indices (*hkl*)	Sin Θ	L (calcd.)	L (obs.)
200	0.12613	...	24.58
220	.17833	34.84	34.88
222	.21853	42.80	42.78
400	.25235	49.56	49.68
420	.28213	55.58	55.63

The data given in Table II show that the sample was located at the center of a perfect arc within the limit of measurement, which from Table I appears to be somewhat less than 0.1 mm. along the film which corresponds to an arc of about 1'30" or about ±0.005 Å. in terms of interplanar distances.

Results.—The alloys examined had the composition indicated in Table VI and were all annealed as previously described. Table III shows the data obtained in the case of one of the alloys. The observed data are compared with values calculated for a face-centered cube and are seen to check within the limit of error in measurement. The sum of the squares of the *hkl* indices of the planes which give lines in the case of a face-centered cube (pure metal) are 3, 4, 8, 11, 12, 16, 19, 20, 24, etc. The number and arrangement of the lines obtained for this alloy are in perfect agreement with the assumption of a face-centered cube.

Table IV shows the results of some intensity measurements made by means of a differential photo-electric photometer built according to a description by Richtmyer. (The author's sincere thanks are hereby expressed to Dr. F. E. Poindexter of the Physics Department of St. Louis

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[5] Clark's nomenclature has been adopted, "Applied X-Rays," McGraw-Hill Book Co., Inc., New York, 1927.

TABLE III

ALLOY 127. COMPARISON OF OBSERVED FILM DISTANCES WITH CALCULATED DISTANCES FOR A FACE-CENTERED CUBE

Equations:[a] $\lambda(h^2 + k^2 + l^2)^{1/2}/2a = \sin\theta$; $\theta = 0.2949L$

Indices (hkl)	Sin θ	L (calculated)	L (observed)
111	0.17320[c]	..	38.8 mm.
200	.20000	39.1	39.2
220	.28280	55.7	55.9
311	.33166	05.7	65.8
222	.34641	68 7	68.6
400	.40000	79.9	
331	.43589	87.6	87.7
420	.44721	90.1	90.2
422	.48990	99.4	99.3

[a] a = 3.555 Å. calculated from L = 33.8 millimeters. [b] Calculated from L = 33.8. [c] Very faint line. Could not measure accurately.

TABLE IV

PHOTOMETRIC DATA

Alloy	Relative densities of lines (Obs.) 111	200	220	311	Density ratios 111/220	111/311
132	10	8.2	4.5	4.2	2.2	2.4
127	10	6.4	4.8	3.5	2.1	2.8
100	10	6.6	4.6		2.2	[a]
Calcd.	10	5.4	4.7	6.5	2.1	1.5

[a] Light film.

University for the use of this apparatus.) A comparison of observed values with values calculated on the assumption of a face-centered cube shows very close agreement.

Table V shows the experimental data obtained for the alloys examined when a stands for the unit cube edge and A stands for the average atomic weight. The calculated values of a were obtained by means of the third equation given in the heading of the table. The values of A used in these calculations were obtained by means of the last equation given in the same heading, which assumes a substitutional solid solution. The values of a observed from the different planes vary among themselves slightly, which is not surprising in view of the fact that we are dealing with a solid solution and hence the distribution of a given kind of atom in the various sets of parallel planes may vary. Also, the calculated values for a are in some cases appreciably larger than the observed values, a possible explanation for which will be offered below.

The observed values of a obtained from the 111 planes are considered most reliable, for in these cases the values of L were obtained by measuring the film distance between corresponding lines on the two sides of the zero beam and dividing the distance by two. The values of L for the other sets of planes were obtained by measuring from the 111 lines and adding to the

TABLE V

COMPARISON OF EXPERIMENTALLY DETERMINED VALUES OF *a* WITH THE CALCULATED VALUES

Equations: $\Theta = 0.2949L;\ \lambda(h^2 + k^2 + l^2)^{1/2}/2 \operatorname{Sin}\Theta = a$ (Exp.)

$$(4 \cdot A \cdot 1.65/\text{Density})^{1/3} = a(\text{calcd.});\ A = \cfrac{100}{\cfrac{\%\ \text{Cu}}{65.57} + \cfrac{\%\ \text{Ni}}{58.68} + \cfrac{\%\ \text{Al}}{27} + \cfrac{\%\ \text{Mn}}{54.93}}$$

Alloy	L in *mm.* 111	L in *mm.* 220	L in *mm.* 311	*a* 111	*a* 220	*a* 311	*a* (calcd.)
104	34.2	56.3	66.2	3.510	3.515	3.525	3.560
105	34.2	55.8	66.1	3.515	3.550	3.530	3.565
106	34.2	56.0	66.5	3.510	3.530	3.505	3.565
108	34.0	56.0	66.0	3 530	3 530	3.535	3.560
109	34 0	56.1	66.4	3.535	3.530	3515	3.605
113	33.9	56.0	66.5	3.540	3.530	3.510	3.560
127	33.8	55.9	65.8	3.555	3.540	3.545	3.560
132	33.9	55.8	65.9	3.545	3.540	3.540	3.570
133	34.1	56.6	67.0	3.520	3.495	3.485	3.565
134	34.2	56.3	66.4	3.515	3.515	3.515	3.560
137	34.1	56.6	66.1	3.525	3.500	3.530	3.570
138	33.7	55.4	65.5	3.570	3.570	3.560	3.580
140	33.8	[a]	[a]	3.555			3.570

[a] Light film.

L value for the 111 planes. The absolute error in measuring the values for L for the 111 planes is thus seen to be one-half that for the other planes.

The observed values for *a* obtained from the 111 planes are shown in Table VI. The values for *a* are compared with the nickel–copper ratio for a constant aluminum content. The cube edge generally increases with rising aluminum content and falls with rising nickel–copper ratio, which in each case is what would be expected if the alloys are solid solution of one kind. In two or three cases the observed values almost reach the calculated values while the others are lower. These facts can be explained if it

TABLE VI

COMPARISON OF OBSERVED VALUES OF *a* WITH CALCULATED VALUES

No.	Mn, %	Al, %	Ni/Cu	*a* (obs.)	a (calcd.)
133	1	2	1.94	3.520	3.565
134	1	2	2.03	3.515	3.560
104	1	2	2.23	3.510	3.560
113	1	2	2.34	3.540	3.560
140	1	3	1.51	3.555	3.570
108	1	3	2.31	3.530	3.560
132	1	4	1.88	3.545	3.570
137	1	4	2.00	3.525	3.570
127	1	4	2.06	3.555	3.560
106	1	4	2.28	3.510	3.560
138	1	6	1.82	3.570	3.580
105	1	6	2.23	3.515	3.565

is assumed that in the case of most of the alloys not all of the aluminum is held in what has been called the a-solid solution. On a few films a few "Extra Lines," *i.* e., lines not belonging to the a-solid solution pattern, were found. The locations of these lines are given in Table VII.

TABLE VII

COMPARISON OF OBSERVED FILM DISTANCES FOR LINES NOT BELONGING TO THE FACE-CENTERED PATTERN OF THE (ı-SOLID SOLUTION WITH CALCULATED FILM DISTANCES FOR SOME POSSIBLE LINES

	Film distances (calculated)					Film distances (observed)				
Form[a]	Al F.C.	Mn 56 atoms	Mn 20 atoms	Al Ni B. C.	Al Cu γ'	104	106	113	100 No Mn	127 un-annealed
a	4.043	8.89	6.289	2.82	8.674					
	(111)				(321)					
	29 67				29.63					29.95
	(200)	(330)	(221)	(110)						
	34.31	3308	3306	34.81						
		(332)	(310)							
		36.61	34.86							
		(510)	(311)							
		39.84	36.59							
					(521)					
					43 93	44.76			43	43.65
	(220)			(200)	(611) (532)					
	48.76			49.45	49.55		50.8	51.0		49.55

[a] All of these are taken as some form of cubic lattice.

Equilibrium Diagram.—Both the photomicrographs and x-ray patterns show conclusively that these alloys are in the main a-solid solution. According to Austin and Murphy,[6] alloys of copper and nickel with up to about 10% of aluminum should form the a-solid solution at temperatures just below the solidus. With alloys higher in aluminum these authors indicated the formation of a eutectic constituted of α- and 0-solid solutions, the β-solid solution resulting from a solution of NiAl and Cu_3Al in each other. Evidence presented by Guillet[7] and the present author indicates that aluminum is less soluble in copper and nickel at lower temperatures, especially when the percentage of copper is lowered. Jette, Phragmen and Westgren[S] did not find evidence for Cu_3Al in copper–aluminum alloys. These authors found aluminum dissolving in copper up to 8% and also evidence for a γ'-phase, the cube edge of which varied from 8.704 to 8.652 Å. for alloys with 16–25% aluminum.

Discussion.—The results shown in Table V seem to indicate that in the case of most of the alloys not all of the aluminum was held in the solid solution. The physical properties of these alloys, photomicrographs and

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[6] Austin and Murphy, J. *Inst. Met.*, 29,327 (1923).

[7] Guillet. Compt. rend., 158, 704 (1914).

[8] Jette, Phragmen and Westgren, J. *Inst. Met.*, 31,193 (1924).

the "Extra Lines" listed in Table VII indicate a second phase of some sort. It might be expected that this second phase would be a solid solution the composition of which is not known at the present time. The "Extra Lines" occur on the films at about the correct positions for a solid solution having a cube edge of 8.674 Å. (see Table VII), which is intermediate between the high and low values given by Westgren for the γ'-phase in copper–aluminum alloys. It might not be unreasonable to expect a similar γ'-phase in nickel-copper–aluminum alloys, since nickel and copper are known to form a continuous series of solid solutions. However, the "Extra Lines" could be almost equally well explained as being derived from solid solutions having, respectively, cube edges of 4.54, 6.42 or 7.51 Å. Which of these, if any, is correct will have to be determined by further work.

Some preliminary results indicate that the cube edges for the unannealed alloys are larger than the values given in Table V for the annealed alloys, indicating more'aluminum held in the a-solid solution in the sand-cast (unannealed) condition than in the annealed condition. This is in agreement with the results obtained from the photomicrographs but is in apparent disagreement with the x-ray evidence for alloy number 127 in which case "Extra Lines" (evidence for a second phase) were found for the unannealed alloy but none for the annealed.

The x-ray study of this alloy system is being continued in order to define more clearly, if possible, the nature and constitution of the second phase, evidence for which has been given. It is also proposed to study some chill-cast alloys of these same compositions, in order to determine whether or not more aluminum is held in solid solution when the alloy is cooled rapidly.

The present study has not thrown any new light on the important influence of the 1% of manganese on the physical properties of these alloys.

Summary

An x-ray study has been made of the constitution of some copper–nickel–aluminum–manganese alloys. Previous work has already indicated that these alloys are in the main a-solid solutions. The present x-ray examination confirms this former finding. Some evidence for a second constituent is presented but complete identification has not yet been made.

ST. LOUIS, MISSOURI

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

THE VAPOR PRESSURE AND CRITICAL TEMPERATURE OF FLUORINE

BY G. H. CADY AND J. H. HILDEBRAND

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The vapor pressure of liquid fluorine has heretofore been known at only one point, the boiling point being given by Moissan and Dewar as approximately −187°.[1] It seemed worth while, therefore, to utilize the equipment and experience available in this Laboratory to determine the vapor pressure of this element over a range of temperatures.

Experimental

Fluorine was generated by the electrolysis of fused potassium bifluoride in an apparatus of the type designed by Argo, Mathers, Humiston and Anderson[2] as modified by Simons.[3] The generator now in use has been further modified by increasing its capacity to 2.4 liters and by casting the vessel with a disk attached to the top rim of the cylinder sufficiently wide to cover the electrical heating coils and their insulating packing The outer edge of the disk was further provided with a vertical rim. It had been found in working with the older form of generator that the electrolyte gradually crept over the rim of the containing vessel and worked down to the heating circuit. The present arrangement successfully prevents this difficulty.

Fluorine from the generator was passed through the copper trap, A (see Fig. 1), which was kept at a temperature of about 86°K. by a bath of liquid air rich in oxygen. This vessel served to remove impurities less volatile than fluorine, which probably were hydrogen fluoride, evolved from the molten bifluoride, fluorides of carbon, from the graphite anode, oxygen and oxygen fluoride[4] produced from traces of water in the electrolyte. Since neither O_2 nor OF_2 could be completely condensed in A, both having appreciable vapor pressures at 86°K., preliminary electrolysis of the molten salt was carried on for several hours, thereby decomposing the dissolved water. Fluorine, which was generated at a rate of about five grams per hour, was passed through the apparatus for thirty minutes, in order to sweep out the enclosed air. At the end of this time, the glass tube at D was sealed shut and gas was condensed in the cylindrical copper bulb, B, which was constantly maintained at the boiling temperature of the liquefied gas. After the desired quantity of liquid had been collected the tube at E was sealed shut. Pieces

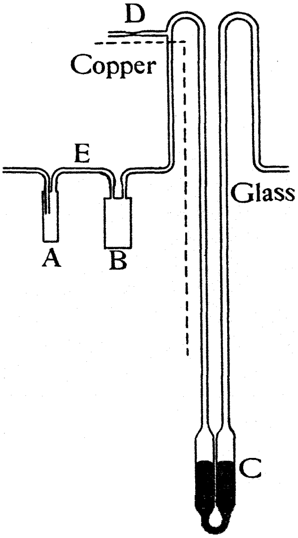

Fig. 1.—Apparatus for measuring the vapor pressure of fluorine.

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[1] H. Moissan and J. Dewar, *Compt. rend.*, 125, 505 (1897).

[2] Argo, Mathers, Humiston and Anderson, Trans. *Am. Electrochem. Soc.*, *35*, *335* (1919).

[3] Simons, THIS JOURNAL, 46, 2175 (1924).

[4] P. Lebeau and A. Damiens, *Compt. rend.*, 188, 1253 (1929).

of small German silver tubing were inserted in the line immediately above B to diminish the heat leak to the liquid fluorine.

C is a glass equalizing mercury manometer of about 1.5 cm. diameter attached to the copper tubing by a copper to glass seal. Since fluorine reacts with mercury. forming a thin skin of mercury fluoride which adheres to the walls of the tube, it was not possible to observe both mercury levels accurately when balancing the air pressure upon the right-hand column against the fluorine pressure on the left. The vapor pressure was, therefore, taken as equal to the air pressure required to bring the mercury surface, in contact with the air, to the position of balance at the start of the experiment. The error in pressure readings, caused by the consumption of mercury during a run, was found to be not more than a millimeter of mercury. Temperatures were read with a copper–constantan thermocouple made from wire kindly furnished us by Professor W. F. Gianque. Since samples of wire from the same spools had been carefully calibrated,[5] we were able to use a thermocouple correct to within 0.05°K. The junction of the thermocouple was soldered to the outside of the bulb, B, at a point near the surface of the fluorine inside.

A Leeds and Northrup type *K* potentiometer was used to measure the e. m f. of the thermocouple. Results were reproducible to about one millionth of a volt, which corresponds on the temperature scale to abuut 0.05".

The bulb, B, was immersed in a liquid-air bath. Various temperatures could be obtained either by changing the composition of the liquid or by lowering the pressure of the gas phase. Constant temperatures could be maintained for sufficient time for the attainment of vapor pressure equilibrium.

When glass bulbs were used for A and B, no two samples of fluorine gave the same vapor pressure curve and their boiling points all increased when part of the liquid was allowed to boil away. Boiling points ranged from 83 to 86°K., and one sample would change as much as from 84 to 85.5°K. while boiling away. All attempts at fractionation failed to give pure products. In spite of these results we had reason to believe that the boiling point of fluorine was near to 84.9°K., because the bath about the condensing gas had to be kept within 0.2° of 84.8°K. while the atmospheric pressure was 76 cm.

When the metal apparatus was used, the first sample of fluorine condensed behaved very satisfactorily. It represented the product of four hours of electrolysis with a current of eighteen amperes and probably amounted to about 18 cc. of liquid. No appreciable change in boiling point could be observed when part of it boiled away. Fully half of the specimen must have been set free during such tests, so we were working with either a constant boiling mixture or pure fluorine. The former state of affairs is very improbable, because the water in the electrolyte had been decomposed by preliminary electrolysis. Not more than traces of oxygen and OF_2 could have been in the fluorine, and our constant boiling point indicates that even these were absent.

Vapor Pressure of Fluorine.—The results are given in Table I. The first column gives the observed temperature in degrees absolute; the second, the observed pressure in centimeters; the third, the pressure calculated by substituting the observed temperatures in the equation given below.

The data are represented by the empirical equation

$$\log_{10}P = 7.3317 - \frac{406.8}{T} - 0.007785T$$

where P is in cm. of mercury and T in degrees Kelvin. No observed point

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[5] Giauque, Buffington and Schulze, THIS JOURNAL, 49, 2343 (1927).

TABLE I

VAPOR PRESSURE OF FLUORINE

T, °K. (obs.)	*P*, cm. (obs.)	P, calcd.	T, °K. (obs.)	P, cm. (obs.)	*P*, calcd.
72 53	14.54	14.41	80.98	48.23	47.59
72 53	14.57	14.41	81.19	49 32	48.85
75.18	21 53	21.65	81.20	49.34	45.92
75 18	21.54	21.65	81.22	49.53	49.04
75.18	21.53	21.65	83 09	61.53	61.55
75.18	21.50	21.65	83.11	61 57	61.67
75.45	22.25	22.50	83.45	64.24	64.20
75.53	22.53	22.78	83.48	64.48	64.38
75.59	22.69	22.99	84.13	68.64	69.35
75.88	23.83	23.99	84.65	73.40	73.50
75 93	24.01	24 16	84.68	74.18	73.78
76.70	27.10	26.97	84.68	73.93	73.78
76.72	27.20	27.03	84.73	74.02	74.19
76.72	26.90	27.03	84.77	73.84	74.55
76.74	27.09	27.11	84.81	74.14	74.85
78.96	36.68	36.76	85.28	78.02	78.95
79.01	36.78	36.99	85.25	78.55	78.62
79.02	36.87	37.01	85.27	79.40	78.85
79.18	37.88	37.80	85.32	79.36	79.35
79.18	37.87	37.80	85.40	79.77	79.87
80.09	43.00	42.58	85.81	84.11	83.56
80.09	43.00	42.58	85.99	85.50	85.20
80.96	48.03	47.48			

departs from this equation by more than 0.1°. The data are plotted in Fig. 2, and the line represents the equation.

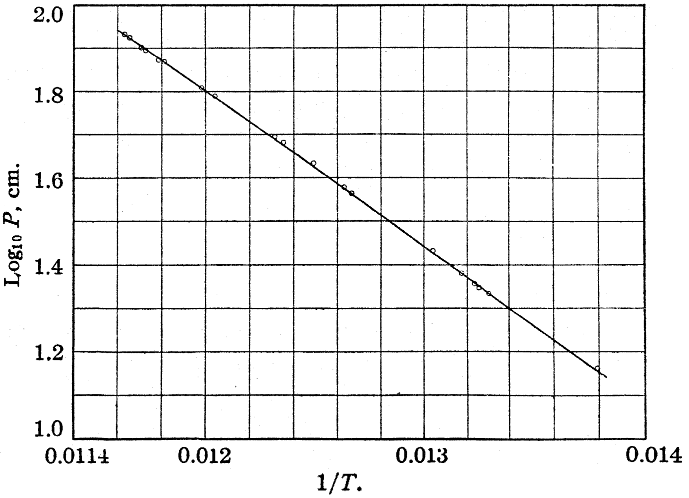

Fig. 2.—Vapor pressure of fluorine.

The boiling point of fluorine is calculated from this equation to be 84.93°K. Taking into account not only the experimental error in our vapor pressure measurements but also the chance that our temperature scale might have been wrong by a few hundredths of a degree, this value is probably correct within 0.1°.

Moissan and Dewar[1] obtained the boiling point by condensing the gas in a glass bulb cooled with liquid oxygen under reduced pressure. They found the minimum reduction of pressure which allowed condensation of fluorine to be 32.5 cm. of mercury and concluded that fluorine boils at −187°C. or 86.1°K. Unfortunately they do not state the atmospheric pressure at the time of this observation, but if we assume that it was 76.0 cm. and employ recent data for the vapor pressure of oxygen,[6] the calculated boiling point is 85.10°K., a figure which is in rather good agreement with our value.

The Critical Temperature of Fluorine.—We have made a few measurements of the critical temperature in a capillary glass tube. Since our previous experience with glass was not very satisfactory, we made no extended efforts to obtain reproducible results. One tube gave 143.3°K., and another, treated more carefully, gave 144.1°K. An approximate value of the critical temperature, is therefore, 144°K.

The critical pressure can be estimated with considerable confidence, since a plot of log P against $1/T$ for related gases shows the critical pressure lying above the vapor pressure line by only about 2 atmospheres.? Using our vapor pressure measurements in this way we get $P_c = 55$ atmospheres

The heat of vaporization of fluorine at the boiling point may be determined, from the slope of the vapor pressure curve given above, to be 1600 cal. per mole. Giauque and Wiebe[S] have found that by substituting the value of P as calculated from Berthelot's equation of state in the equation of Clapeyron, a closer approximation to the calorimetric heat of vaporization of hydrogen chloride is obtained than one gets from the slope of the vapor pressure curve. From our value for the critical temperature and from the density of liquid fluorine as given by Moissan and Dewar[1] we have made a similar calculation. The results at the boiling point are A H = 1540 cal. and A S = 18.1.

Summary

1. Measurements of the vapor pressure of fluorine have been made between 15 and 86 cm. which are closely given by the equation

$$\log_{10}P(\text{cm.}) = 7.3317 - \frac{406.8}{T} - 0.007785T$$

2. The boiling point is calculated to be 84.93°K.

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[6] Cath. *Comm.* Phys. *Lab. Univ. Leiden*, No. 152 (1918).

[7] J. H. Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, 1924, pp. 32–34.

[8] Giauque and Wiebe, THIS JOURNAL, 50, 101 (1928).

3. The critical temperature is approximately 144°K. and the critical pressure is about 55 atmospheres

4. The heat of vaporization at the boiling point is 1600 cal. per mole, as calculated by the Clausius–Clapeyron equation, or, allowing for deviations from the gas laws, 1540 cal.

BERKELEY, CALIFORNIA

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

FREEZING POINTS OF THE SYSTEM WATER–HYDROGEN FLUORIDE

BY G. H. CADY AND J. H. HILDEBRAND

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The highly polar nature of both water and hydrogen fluoride suggested that an especial interest would attach to a determination of the solid compounds they might form with each other. We wished particularly to learn whether any of these might be regarded as resulting from the partial substitution of water in the polymer $(HF)_6$, which Simons and Hildebrand[1] assumed to explain the vapor densities of hydrogen fluoride over a considerable range of pressure and temperature. In spite of the excellent agreement of the assumption with the data, it is quite possible that the association actually involves more numerous molecular species, one of which might be $(HF)_4$, which has been proposed by Berliner and Hann.[2] They point out that the hydrofluorides of amines have the general formula $B \cdot 4HF$ in which B stands for the molecular formula of the base. Other compounds such as $KF \cdot 3HF$ and $MgF_2 \cdot 2NaF$ may be regarded as derivatives of the hypothetical acid H_4F_4. If water behaves in a manner similar to the amines, one compound formed should be $H_2O \cdot 4HF$.

Although no complete study of the system $HF–H_2O$ has previously been made, the freezing points of hydrogen fluoride,[3] of the compound $H_2O \cdot HF$,[4] and of dilute hydrofluoric acid solutions in concentrations ranging up to 4.140 molal[5] have been known for several years. Mr. L. Clark, working in this Laboratory during 1938, made a partial investigation of the system. but his work was considered of too preliminary a nature to warrant publication

Experimental Part

The apparatus used is illustrated in Fig. 1. The equilibrium mixture was contained in a gold cup of about 175-cc. capacity. This was surrounded by a taller copper cup

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[1] Simons and Hildebrand, THIS JOURNAL, 46, 2183 (1024).

[2] J. F. T. Berliner and R. M. Hann, *J. Phys. Chem.*, 32, 1142–1162 (1928).

[3] Simons, THIS JOURNAL, 46, 2179 (1924).

[4] R. Metzner, *Compt. rend.*, 119, 682 (1894).

[5] Paterno and Peratoner, *Atti Accad. Lincei*, 6, 306 (1890); Kendall, Booge and Andrews. THIS JOURNAL, 39, 2303 (1917); Anthony and Huddleston, *J. Chem. Soc.*, 127, 1122 (1925).

which fitted closely into a small Dewar cylinder, thereby partially protecting the glass against attack by hydrofluoric acid vapor. To afford still further thermal insulation, the small Dewar was placed within a one-gallon vacuum jar. Both vessels had covers of light wood provided with suitable holes for the introduction of the gold-plated stirrer, the platinum pipet for removing samples for analysis, and the thermocouple, which was encased in a platinum tube. The pipet had a capacity of about 10 cc. and was equipped at the bottom with a filter of platinum gauze and spongy platinum.

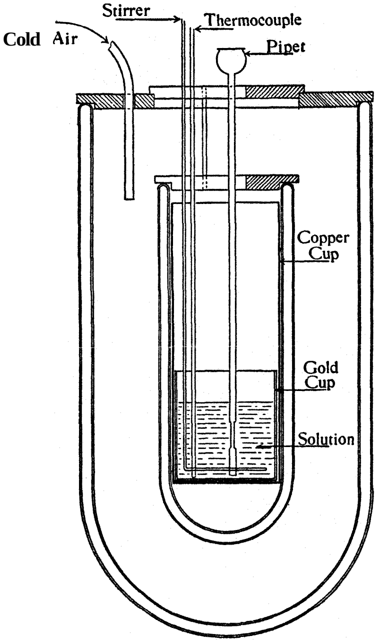

Fig 1.—Apparatus for determining freezing points of aqueous hydrogen fluoride solutions.

For solutions of smaller concentration than 0.51 mole fraction of HF, Baker and Adamson's C. P hydrofluoric acid was used. To obtain more concentrated acid, it was necessary to decompose KHF_2 by heating."

The following simple procedure was found to give reproducible freezing points over most of the range. To about 100 cc. of solution in the gold cup, enough liquid air was added to partially freeze the solution. After stirring continually for about fifteen minutes to allow the attainment of equilibrium between solid and solution, the temperature was read, and immediately afterward a sample of the liquid phase was removed in the pipet. This sample, usually from 1 to 5 cc., was dissolved in water contained in a paraffin bottle and its weight determined by difference. A titration of the acid in this dilute solution with sodium hydroxide then gave the composition of liquid in equilibrium with the frozen solid at the observed temperature. Following the suggestion of Haga and Osaka,[6] phenolphthalein was used as the indicator.

For mole fractions of hydrofluoric acid between 0.68 and 0.89. the above treatment did not give very reproducible results. The crystals of solid seemed to be so small that they clogged the filter in the pipet and prevented the removal of large enough samples of solution. It was, therefore, found necessary to determine warming curves and to take the final sudden change in slope as the freezing point. An analysis of the completely liquid solution then became an easy matter.

Table I gives the experimental points, and they are plotted in Fig. 2.

TABLE I

FREEZING POINTS OF THE SYSTEM $HF-H_2O$

Mole fraction, HF	Temp., °K.	Solid phase	Mole fraction, HP	Temp., °K.	Solid phase
0.00777	272.10	Ice	0.698	197.6	$H_2O \cdot 2HF$
.0564	266.7	Ice	.710	197.3	$H_2O \cdot 2HF$
.0809	263.2	Ice	.743	191.3	$H_2O \cdot 2HF$
.1565	250.0	Ice	.762	181.9	$H_2O \cdot 2HF$
.216	231.6	Ice	.776	171.7	Eutectic
.265	213.0	Ice	.786	172.3	$H_2O \cdot 4HF$

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[6] Haga and Osaka, J. *Chem. Soc.*, 67, 251–255 (1895).

Table I *(Concluded)*

Mole fraction, HF	Temp., °K.	Solid phase	Mole fraction, HF	Temp., °K.	Solid phase
0.276	202.9	Eutectic	0.796	172.7	$H_2O{\cdot}4HF$
.307	210.3	$H_2O{\cdot}HF$	(.800)	(172 8)	$H_2O{\cdot}4HF$
.321	213.6	$H_2O{\cdot}HF$	.817	172.4	$H_2O{\cdot}4HF$
.371	224.1	$H_2O{\cdot}HF$	.864	167.6	$H_2O{\cdot}4HF$
.403	229.5	$H_2O{\cdot}HF$	.883	162.2	Eutectic
.478	236.9	$H_2O{\cdot}HF$	.894	166.1	HF
(.500)	(237.7)	$H_2O{\cdot}HF$	.913	173.3	HF
.515	237.2	$H_2O{\cdot}HF$	.939	179.4	HF
.575	231.5	$H_2O{\cdot}HF$	.961	184.1	HF
.627	222.0	$H_2O{\cdot}HF$	.974	186.1	HF
.675	204.9	$H_2O{\cdot}HF$	.982	187.6	HF
.685	197.9	$H_2O{\cdot}HF$ and $H_2O{\cdot}2HF$	1.000	190.1[3]	HF

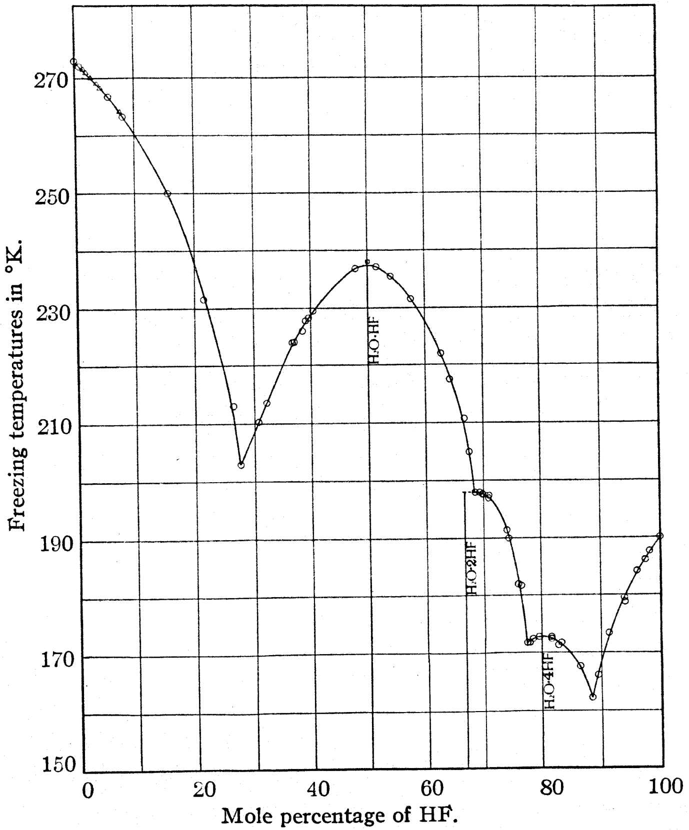

Fig. 2.—Freezing points of aqueous solutions of hydrogen fluoride. Circles refer to this research, the square to Metzner[4] and the triangles to Anthony and Huddleston.[5]

Three distinct addition compounds are indicated by the curve: $H_2O·HF$, $H_2O·2HF$ and $H_2O·4HF$. The second does not quite melt congruently, but the shape of the curve hardly leaves any doubt that it has the composition given. The first of these has been prepared by Metzner[4] by freezing it from hydrofluoric acid solutions. He reports its melting point to be −35°, which is not far from our value, −35.4".

Before anything very definite can be said concerning the configuration of these compounds, it will be desirable to have data bearing upon their crystal structures. We will merely call attention to the fact that the observations of Berliner and Hann[2] are extended by the discovery of the compound $H_2O·4HF$ and that the existence of two compounds with an excess of HF, while there are none with an excess of H_2O, harmonizes with the view that HF tends to assume a more complex polymerization than water.

Summary

The freezing point-composition diagram for the system water–hydrogen fluoride has been studied over the entire range. In addition to the solid compound $H_2O·HF$, previously known, we have discovered the compounds $H_2O·2HF$ and $H_2O·4HF$.

BERKELEY, CALIFORNIA

[COMMUNICATION NO. 430 FROM THE KODAK RESEARCH LABORATORIES]

MEASUREMENTS OF THE FLUORESCENCE OF CELLULOSE ACETATE, CELLULOSE NITRATE AND GELATIN IN ULTRAVIOLET LIGHT

BY JAMES G. MCNALLY AND WALDEMAR VANSELOW

RECEIVED JUNE 11, 1930 PUBLISHED OCTOBER 6, 1930

The fluorescence of cellulose in ultraviolet light was first noted by Hartley[1] in 1893 but no further attention seems to have been given the subject until Judd-Lewis began a series of experiments in 1918. In his first communication, Judd-Lewis[2] described the appearance of various cellulosic derivatives when held where the photographic plate is normally placed in a quartz spectrograph. Cellulose acetate, viscose, filter paper and "normal" paper showed strong fluorescence in the ultraviolet region while nitrocellulose and paper treated with ethyl malonate showed very little fluorescence.

A method of photographing the fluorescent spectrum was devised by this author[3] in which a camera was mounted in the back of the spectrograph arm and the spectrum photographed by reflected light, a procedure necessi-

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[1] W. N. Hartley, J. *Chem. Soc.*, 63, 243 (1893).

[2] S. Judd-Lewis, J. *Soc. Dyers Colourists*, 34, 167 (1918).

[3] S. Judd-Lewis, *ibid.*, 37, 201 (1921).

tated by the opacity of the materials under investigation. The densities of the spectral lines obtained on the plate were compared with the corresponding lines of an arbitrarily chosen standard paper, the specifications for which are not given. It is not possible, therefore, for other workers to compare their results with those of Judd-Lewis, but a qualitative idea of some of his results may be gained. Various types of filter paper were found to give divergent results and no relation was observed to exist between the fluorescent power and any other property of the paper. It was certain, however, that moisture content had little to do with the phenomenon. The fluorescence of hydrocellulose increased markedly as the period of time the pulp was left in the beater increased, the most rapid rate of change taking place in the interval between two and three hours' beating. This might be taken to mean that ultraviolet fluorescence increases as the molecular degradation of cellulose proceeds, which cannot be true without limits because the ultraviolet fluorescence of glucose is less intense than that of cellulose.

In the last papers by Judd-Lewis[4] a description was given of the fluorescent spectrum of a large number of cellulose products examined in a tungsten arc lamp. It was shown that fluorescence was excited by all the wave lengths present below $\lambda 330$ mμ. The physical condition of the specimen seemed to play no part in determining the fluorescent spectrum, as a comparison of data obtained with the same cellulose acetate in the form of a powder, a paper and a transparent film showed little if any difference. The fluorescence did appear to be sensitive to slight chemical changes, as cellulose, hydrocellulose and oxycellulose could be easily distinguished by this means.

Pringsheim and Gerngross[5] have reported that the fluorescence in ultraviolet light of a number of organic polymers—lichenin, cellulose, glycogen, inulin, acetate, gelatin, etc.—increased as the colloidal material was disgregated. The observations were made visually and it was suggested that this property of organic colloidal materials in general might be used to characterize their state of aggregation.

Data of a conflicting nature were obtained by the present authors while attempting to use this property of cellulose acetate to indicate something about the micellar structure of the material. Visual evidence was obtained that the physical structure of the substance was related to its fluorescent power and that marked changes in colloidal properties might be accompanied by no variation in fluorescent properties. The quantitative experiments described in this paper were carried out to determine what relation, if any, existed between the physical and colloidal structure and fluorescent properties of cellulose acetate and cellulose nitrate and gelatin.

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[4] S. Judd-Lewis, *J. Soc.* Dyers *Colourists*, 38, 99 (1922); 40, 29 (1924).

[5] *H.* Pringsheim, and O. Gerngross, *Ber.*, 61, 2009 (1928).

The Fluorescence of Cellulose Acetate and Cellulose Nitrate Films

Method of Measurement.—When the image of a mercury arc spectrum is focused on a film of cellulose acetate, the lines of the spectrum are visible in a dark room down to **A241** mμ. The region from **A241** mμ to *365* mμ is so far below the limit of visual perception that no question exists but that the visible light is fluorescent light excited by the ultraviolet. The fluorescent radiation is gray-blue in color and the color is independent of the frequency of the exciting radiation. The fluorescence is not polarized and is passed with high intensity by the K2 Wratten filter but is almost completely absorbed by the **K3** filter, which fact places the wave length of the light emitted as between **A485** mμ and *505* mp, the limits for 60% transmission for the **K2** and **the K3** filters, respectively.

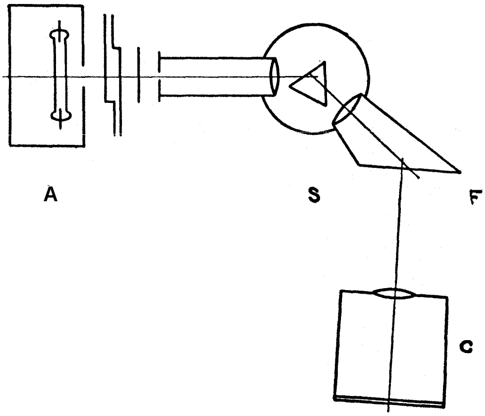

Fig. 1.—Apparatus for measuring fluorescence in films.

The apparatus used to record the fluorescent light emitted by the cellulose acetate films is indicated by the diagram in Fig. 1.

Light from the Cooper-Kewitt quartz mercury arc **A** was resolved by the Gaertner quartz spectrograph S and images of the slit formed on the film under investigation at F. The fluorescent image was photographed by the camera C. The lamp was operated at 155 volts. Using an f 4.5 lens in the camera and Eastman Speedway plates, a suitable time of exposure was found to be forty minutes. The plates were all developed in metol-hydroquinone process developer to a gamma of one.

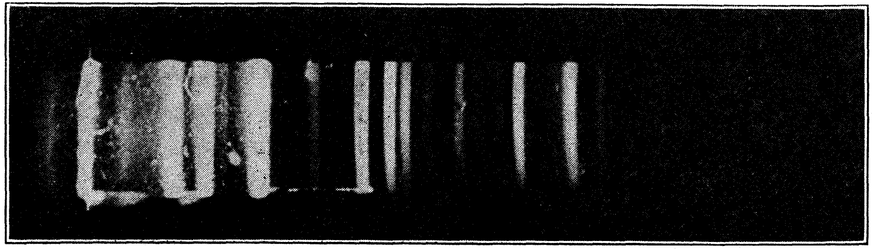

Fig. 2.—Fluorescence of cellulose acetate in the mercury arc spectrum.

Figure 2 is a photograph of the fluorescent light excited by ultraviolet radiations falling on a film of cellulose acetate. To compare the fluorescence of different samples, the densities of the lines in this plate were measured by a micro-densitometer and compared with the densities of the lines obtained by making a direct photograph of the ultraviolet spectrum by placing the photographic plate at F, the time of exposure being one-tenth of a second. The ratio density of fluorescent line to density of spectral line was plotted against the wave length of the exciting radiation. This ratio approaches proportionality to intensity of fluorescent light/intensity of incident light so long as the exposures are low, but as either or both exposures increase, it becomes more nearly proportional to $(P_1 \log I_1)/(P_2 \log I_2)$ where P_1 and P_2 are the Schwarzschild coefficients for the respective wave lengths of fluorescent and incident light. This ratio will be noted hereafter as R.

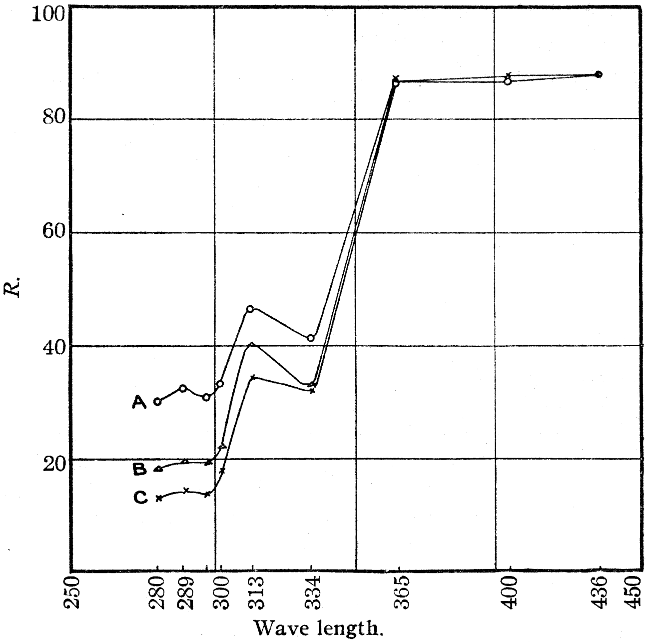

Fig. 3.—Fluorescence of cellulose nitrate films: A, not stretched; B and C, stretched.

Relation between Structure and Fluorescence in Cellulose Nitrate Films.—The curves shown in Fig. 3 were constructed in the manner indicated above and show the fluorescence of three sheets of cellulose nitrate film prepared from the same solution of the original cellulose nitrate. It is evident from the figure that in the region of λ280 to 334 mμ there exists a marked difference in the fluorescent powers of the films forming the order A, B, C, in their ability to fluoresce in this spectral region. The film that showed the fluorescence described by Curve A was formed by evaporating the cellulose nitrate dope to dryness on a glass plate. The other two films were removed from the plate on which the dope was coated while they still contained about 15% of solvent and were further cured while held under tension from two ends, the film represented by Curve C being under higher tension than the film B. It has been shown by one of the present authors and S. E. Sheppard[K] that the tensions on a colloidal film during drying alter the micellar orientation of the film to such an extent that films may be prepared showing the typical optical properties of different crystallographic systems. The film **A** behaves optically as a section of a uniaxial crystal cut perpendicular to the optical axis while the films B and C behave as biaxial films, C being more highly anisotropic than B. It has been shown that the micellar orientation of the film[6] determines its optical properties and it must now be concluded that the ultraviolet fluorescence of the film is also related to its micellar structure.

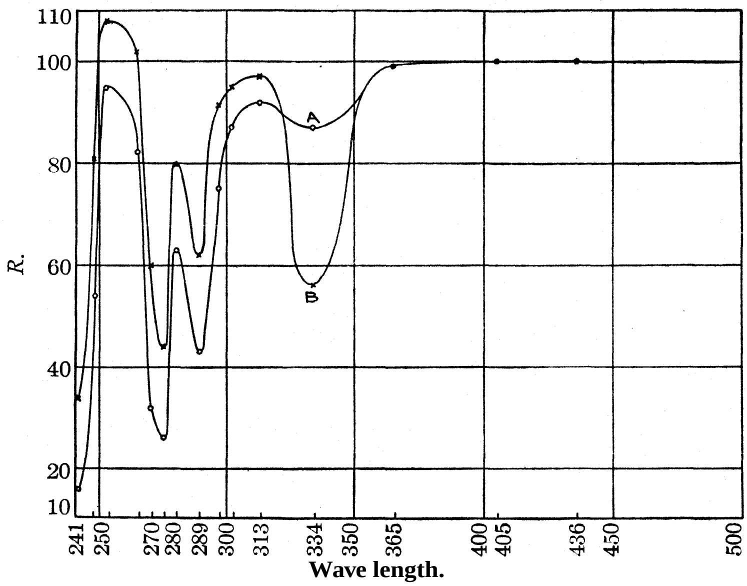

Fig. 4.—Fluorescence of cellulose tri- and diacetate films: A, cellulose triacetate; B, cellulose diacetate.

Fluorescence in Cellulose Acetate Films.—Before proceeding with an examination of the fluorescence of a large number of cellulose acetate films, it was first ascertained that variations in the thickness of the film within wider limits than encountered with our specimens produced very little change in the photograph of the fluorescent light. **A** comparison of the fluorescence of two films of the same material, one **0.16** mm. thick and the

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[6] J. *G.* McNally and S. E. Sheppard, J. *Phys. Chem.*, 34, 165 (1930).

other 0.08 mm. thick, showed a difference in the R ratio of less than 3% at any value for λ.

The fluorescence excited on cellulose triacetate and diacetate films show points of similarity and of difference. In Fig. 4 the curve A represents the fluorescence of a chloroform-soluble triacetate while B was obtained from an acetone-soluble diacetate, both films being optically uniaxial. The two curves have the same general shape but the fluorescence of the diacetate falls below that of the triacetate at λ334 mμ. The curves in Fig. 5 show that this change in fluorescence is a progressive one as a triacetate is hydrolyzed to a diacetate. The data plotted in this figure were taken from samples obtained during an acid hydrolysis of a first stage dope, the samples A, B and C having acetyl values of 40, 37 and 35% and acetone viscosities of 50, 75 and 200 seconds, respectively. By milder treatment in acetylation and second stage hydrolysis, cellulose acetates may be prepared with the same acetyl values as any of the above samples but having higher acetone viscosities. The film D was made from an acetate prepared under such conditions; its acetyl value was 41% and acetone viscosity 600 seconds. When the fluorescence curve for this film is compared with the others in Fig. 5, it is seen more closely to resemble the acetate with the nearest acetyl content rather than the one most closely like it in viscosity, indicating that the chemical constitution, that is, the percentage acetyl-

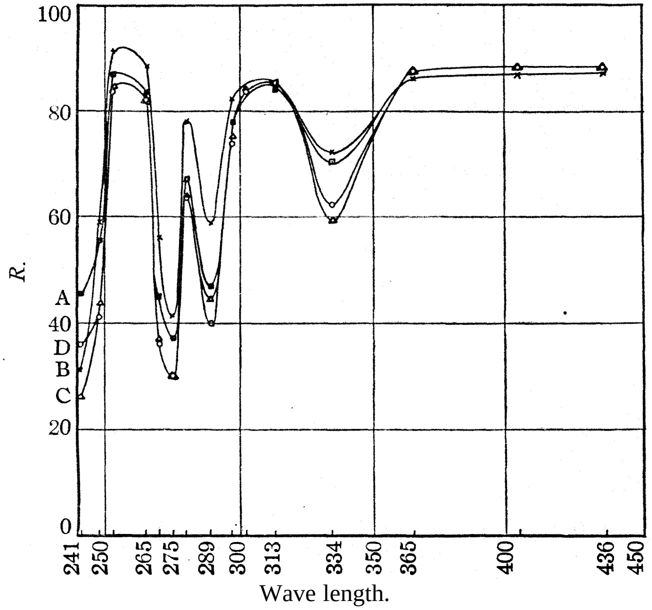

Fig. 5.—Fluorescence of cellulose acetate films of different acetyl content.

ation, is a more important factor in determining the fluorescence of the material in ultraviolet light than any loosening of secondary valency forces caused by the second stage hydrolysis, or eventual depolymerization.

Divergent results were obtained when the fluorescences of stretched and unstretched films were compared in the case of two different acetates. In Fig. 6 the data show that the stretched film B fluoresces more strongly than the unstretched film A and the difference is particularly marked in the region of λ334 mμ. The data from the second acetate plotted in Fig. 7 indicate that in this case the unstretched film A is more strongly fluorescent than the stretched film B and here the difference is most pronounced from λ265 mμ to 300 mμ. The two acetates were typically the same, having similar viscosities and both approximating the acetyl content required for a diacetate. We know of no difference in the properties of the two materials that would account for this difference in their fluorescent power.

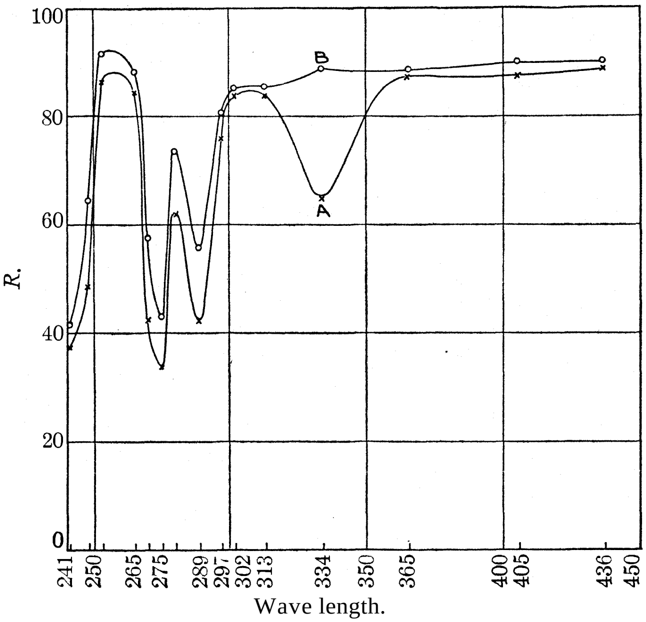

Fig. 6.—Fluorescence of cellulose acetate films: **A,** not stretched; B, stretched.

Fluorescence in Solutions of Cellulose Acetate.—In a well darkened room, solutions of cellulose acetate can be seen to fluoresce when irradiated by ultraviolet light. The fluorescence can be observed to increase in intensity as the concentration of cellulose acetate in the solution increases; but even in the case of a 15% solution, we were unable to photograph the spectrum of the fluorescent light by means of a Gaertner quartz spectrograph after four hours' exposure. We have, therefore, excited fluorescence in the solutions by monochromatic radiation and measured the fluorescent light given off. Figure 8 is a diagram of the apparatus used for this purpose. Light from the quartz mercury arc lamp **A** passed through the quartz windowed water cell W, and 18A Wratten filter, F, and illuminated the slit S_1 of a Bausch and Lomb quartz monochromator, the optical parts of which are indicated by the lenses L_1, L_2 and the prism P. The solution being investigated was placed in an 11-mm. quartz absorption cell C which was enclosed in a light-proof box B. The shutter E opened adjacent to the monochromator slit S_2. The Wratten filter K2 and the photographic plate

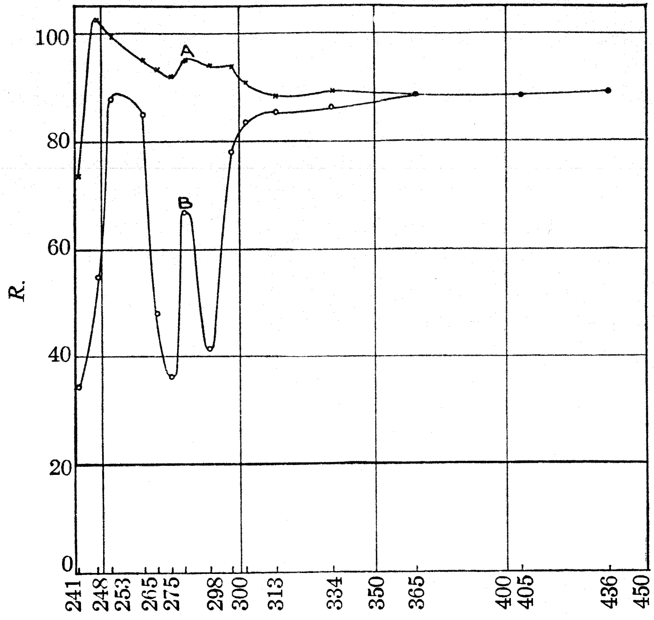

Fig. 7.—Fluorescence of cellulose acetate films: A, not stretched; B, stretched.

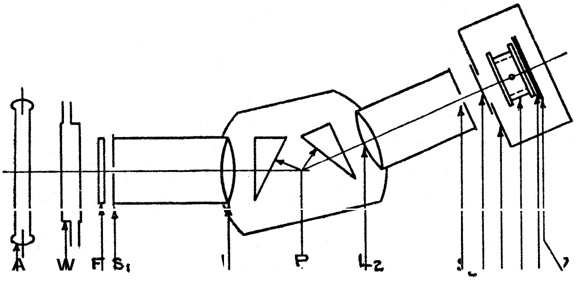

Fig. 8.—Apparatus for measuring fluorescence in solutions.

D were placed in contact with the side of the cell away from the slit. The K2 filter was found to absorb the ultraviolet light completely and transmit the fluorescent light in the case of the solutions used as well as the solid film.[7] Satisfactory plates were obtained with a 15% gelatin solution after a forty-five minutes' exposure, the plates being developed as before to a gamma of one. The densities of the plates were measured by means of the densitometer described by Capstaff[8] and the fluorescent power of the solutions compared on this basis.

The fluorescence of 15% acetone solutions of four cellulose acetates differing in their properties by very wide limits was determined by the method outlined above and the data obtained assembled in Table I. The figures in the first line refer to ball drop viscosity tests. The next line gives the percentage of acetyl group combined, and the final one, the density of the photograph of the fluorescent light after forty-five-minutes' exposure.

TABLE I

THE FLUORESCENCE OF CELLULOSE ACETATE SOLUTIONS

Sample no.	**A**	**B**	**C**	**D**
Viscosity	500	20	20	8
Acetyl, %	40	40	37.8	37.5
Density	0.36	0.40	0.42	0.42

Prom a consideration of the above data it appears that there is no relation between the state of aggregation of the micelles in a cellulose acetate solution and their fluorescence in ultraviolet light of wave length 365 mμ.

The Fluorescence of Gelatin Solutions.—The circumstance that films made from partially broken down gelatin are so brittle that they cannot be handled conveniently makes it a matter of great difficulty to investigate the relation between fluorescence and state of polymerization in gelatin film. We have, however, made such a study of gelatin sols using the same procedure that was outlined for use with the cellulose acetate sols.

A 10% solution of de-ashed gelatin was made up having a PH of 5.2. The flask containing this solution was fitted with a reflux condenser and the solution boiled for twenty-four hours. Samples were taken from time to time and measurements made of the viscosity and fluorescence of the solution. Table II is a summary of these results, the density being, as before, the photographic density caused by the fluorescent light on forty-five-minutes' exposure. The viscosity measurements were made by Dr. Robert Houck and are reported in centipoise units at 40°.

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[7] Aesculin and a number of glass filters were substituted for the K2 but while they had the proper adsorption limits, they fluoresced to a considerable extent in ultraviolet light and were unsuitable for the purpose at hand. No satisfactory substitute was found for the K2 filter.

[8] J. G. Capstaff, *Trans. Soc. Mot. Pict. Eng.*, **11**, 607 (1927).

TABLE II

THE FLUORESCENCE OF HYDROLYZED GELATIN

Hours boiled....	0	0.33	0.55	1.33	2.25	5.00	24.00
Viscosity......	17.8	14.5	11.5	7.6	5.1	2.4	1.55
Density........	0.88	0.72	0.72	0 70	0.60	0.58	0.74

Sheppard and Houck[9] have concluded that diminution of the viscosity of gelatin sols by heating at elevated temperatures is to be accounted for by hydrolytic decomposition of the gelatin. The part of the hydrolysis reaction that causes the reduction of the viscosity, probably by the breakdown of large colloidal molecules, was complete in our experiment in the first five hours of heating and during this period the fluorescence of the sol in ultraviolet light showed a progressive decrease. In the interval between five and twenty-four hours, the solution became amber colored and the fluorescence makes a marked regain toward its initial value. No sensible change in viscosity took place during this time so it seems evident that the increased fluorescence must be associated with changes other than those of micellar nature that might be expected to alter the flow characteristics of the sol.

Discussion of Results

The results of this investigation are not in accord with the conclusions of previous experimenters that the fluorescence of cellulose derivatives is independent of the physical form of the material and related only to changes in chemical composition, and that the fluorescence of gelatin in ultraviolet light becomes more intense as the material is subjected to progressive disgregation. Enough data have been presented in the present paper to prove that: (a) the fluorescence excited by ultraviolet light in cellulose acetate and nitrate films depends on the micellar structure of the film; (b) when the micellar structure is similar, acetates resemble each other in fluorescence when they are alike in chemical composition rather than in colloidal properties; (c) the fluorescence of cellulose acetate sols is independent of the colloidal properties of the sol; (d) the fluorescence of gelatin sols decreases during the part of the hydrolysis causing a change in micellar magnitude and increases later because of some secondary change.

It seems likely that the amount of strain in a cellulose acetate or nitrate film affects the fluorescence of the film and that the effect is different for cellulose ester films made from different materials. The "temporary dichromatism" observed by Kundt[10] and quantitatively investigated by Pulfrich[11] in the case of stretched rubber affords an interesting suggestion as to the cause of the observed change in fluorescence in stretched cellulosic

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[9] S. E. Sheppard and R. C. Houck, *J. Phys. Chem.*, 34,273 (1930).

[10] A. Kundt, Ann. Physik, Old Series, [1] 151,125 (1874).

[11] C. Pulfrich, *ibid.*, New Series, 14,193 (1881).

films. If the absorption coefficients for different wave lengths in the ultraviolet shift independently of each other as a cellulose acetate or nitrate film is stretched, as they do in the visible region in the case of rubber, the amount of fluorescent light emitted by these wave lengths would vary as the energy absorbed varied. It is planned to investigate this matter further.

The evidence seems conclusive that as far as the λ365 mμ is concerned, the fluorescence of gelatin in ultraviolet light decreases as the aggregates responsible for the high viscosity of the sol are broken up. The subsequent increase in fluorescence is connected with some other change in the solution. The darkened color of the solution suggests that humin formation accompanied by partial oxidation and carbonization had taken place. Brooks[12] has remarked that the formation of fluorescent material is almost universally observed when organic material is partially carbonized by heat, which indicates an explanation for our observed rise in the fluorescent power of the solution.

Summary

The intensity of fluorescence of cellulose nitrate and acetate films in ultraviolet light depends on the wave length of the exciting radiation, and the chemical composition and the micellar structure of the film. The intensity of fluorescence of acetone solutions of cellulose acetate in light of wave length 365 mμ is independent of the colloidal properties of the solution. A decrease in the viscosity of gelatin solutions caused by hydrolytic disgregation of micellar structures is accompanied by a decrease in the intensity of fluorescence in light of wave length 365 mp. Subsequent chemical changes cause an increase in the fluorescence.

ROCHESTER, NEW YORK

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[12] B. T. Brooks, "Non-Benzenoid Hydrocarbons," The Chemical Catalog Company, New York, 1922, p. 549.

[CONTRIBUTION FROM THE LABORATORY OF INORGANIC CHEMISTRY, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

AMMONATES OF COPPER SELENATE[1]

BY LOREN C. HURD AND VICTOR LENHER

RECEIVED JUNE 23, 1930 PUBLISHED OCTOBER 6, 1930

Certain of the metallic salts which form complex addition products with ammonia have been subjected to numerous investigations on the part of several workers of the past. Outstanding is the work of Alfred Werner and his students on the preparation and study of the members of the cobalt and platinum systems. In contrast to the cobalt ammines, which are for the most part relatively stable, there exists another class of compounds, the ammonates, which are relatively unstable and which may be represented by the general formula $MA \cdot xNH_3$. As a part of the study of selenium and its compounds carried out at this Laboratory, it was thought that an investigation of the compounds formed by the action of ammonia on the metallic selenates and selenites might yield results of interest. The present report deals with the compounds formed by the addition of ammonia to copper selenate.

Dennis and Koller[2] prepared three ammonates of copper selenate, two of which were products resulting from the partial decomposition of their primary salt, $CuSeO_4 \cdot 4NH_3 \cdot H_2O$. The method utilized by these workers was to pass ammonia gas into a solution of copper selenate to which had been added an excess of ammonium hydroxide. After the ammonia had been passed into the solution for about two hours, clusters of dark blue crystals separated. The product was washed twice with ammonia solution and dried over lime for two hours. Analysis of the material yielded results in accord with the formula ascribed to the tetrammonate monohydrate. Finely ground crystals of the salt were dried in the air for two hours. Ammonia was lost and the resulting pale blue compound was found to be $CuSeO_4 \cdot 3NH_3 \cdot H_2O$. Crystals of the tetrammonate monohydrate were desiccated over lime at a pressure of 25 mm. of mercury for one week. Analysis of the resulting compound showed that one molecule of water had been lost with the formation of the tetrammonate, $CuSeO_4 \cdot 4NH_3$. Willy Lange[3] has recently reported the formation of an ammonate of copper selenate corresponding to the formula $CuSeO_4 \cdot 4NH_3 \cdot 2H_2O$. The method of preparation was not stated. The product was described as a very solu-

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[1] Abstracted from a portion of a thesis submitted to the faculty of the Graduate School, University of Wisconsin, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1939. The thesis was started under the direction of the late Victor Lenher, continued under the supervision of the late George Kemmerer and completed under the guidance of Professor V. W. Meloche.

[2] Dennis and Koller, THIS JOURNAL, 41, 949 (1919).

[3] Willy Lange, Ber., 59, 2113 (1926).

ble, sky-blue crystalline material. The author states that the compound lost water to give the tetrammonate—a blue-violet product. The tetrammonate upon heating decomposed without melting to give the green diammonate. Identification of the tetrammonate is based on one copper determination. No analysis is reported for the diammonate.

Materials

Selenic acid was prepared from purified selenium dioxide by direct chlorination of a 10% solution of selenious acid, according to the method of Metzner.[4] The resulting selenic and hydrochloric acid mixture was neutralized with basic copper carbonate, the solution filtered, and the bulk of the copper selenate isolated from the copper chloride by means of precipitation with ethyl alcohol according to the method of Lenher and Kao.[5] Following four or five precipitations of the selenate by means of alcohol the material was twice recrystallized from water. Chlorides were shown to be absent by testing a 1% nitric acid solution of one gram of the copper selenate with a few cc. of saturated silver selenate solution. Failure of a turbidity or opalescence to appear was taken as evidence of the absence of appreciable amounts of chloride.[6]

The ammonia used throughout this work was obtained for the most part from the National Ammonia Company. The commercial material was transferred into a small iron tank containing sodium. Gas used for the preparation of the ammonates described was obtained by distillation from the dry liquid.

Analytical Methods

Selenium.---Selenium was determined according to the method of Lenher and Kao[7] as described by Hoffman and Lenher?

Copper.—Copper selenate when ignited in a porcelain crucible over a Bunsen burner leaves a residue of copper oxide. The selenium is volatilized as the dioxide. In the case of the ammonates of copper selenate the direct immediate ignition must be avoided because of the reducing action of the ammonia on the copper residue at high temperatures. Consequently it is necessary first to drive off most of the ammonia at a low heat, and then to follow the preliminary heating by a gentle ignition. The temperature of the crucible is then raised to the full heat of the burner. If the preliminary heating is not sufficiently slow, the results obtained will be erratic and the crucible will become stained with a rose-colored deposit produced by the action of metallic copper or cuprous oxide on the glaze of the crucible.

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[4] Metzner, Ann. *chim. phys.*, 15,203 (1898).

[5] Lenher and Kao, THIS JOURNAL, 47,1521 (1925).

[6] Chung Hsi Kao, B.S. thesis, University of Wisconsin. 1924. Dr. Kao states that the sensitivity of this test is limited only by the solubility of silver chloride in water.

[7] Lenher and Kao, THIS JOURNAL. 47, 769 (1925).

[8] Hoffman and Lenher, *ibid.*, 51,3178 (1929).

That the method of ignition is satisfactory for the determination of copper oxide in compounds of the type to be described was demonstrated by numerous analyses, the following two of which may be considered representative.

Compound	CuO, Calcd., %	CuO found %	Detns.	Max. dev.,
$CuSeO_4 \cdot 5H_2O$	26.79	26.73	3	0 14
$CuSeO_4 \cdot 3NH_3 \cdot H_2O$	28.85	28.92	3	0.07

In cases where because of small amounts of sample or difficulty in weighing, it was desirable to estimate the copper content of the filtrate from the selenium determination, the determination was made according to the sulfocyanate method of Rivot[9] as modified by Treadwell.[10]

Ammonia.—Ammonia was determined by distillation of the gas from an alkaline solution which had been freed from copper. In the course of an investigation of the copper sulfate complexes, Horn and Taylor[11] experienced considerable difficulty in the direct distillation of ammonia from alkaline solutions of the ammonates. These workers found that when sodium hydroxide is added to a solution containing appreciable amounts of copper sulfate, the ammonia is expelled with difficulty and prolonged boiling is necessary to drive over the last traces of ammonia. In all cases they found that it was necessary to distil until the residue in the Kjeldahl flask had evaporated almost to dryness in order to arrive at quantitative results.

it was found that copper selenate behaves in a like manner. Because of this difficulty it was considered necessary to remove the copper from the solution before distillation. This was accomplished by warming the sulfuric acid solution of the ammonate with a piece of metallic aluminum. The copper was quantitatively deposited along with a portion of the selenium. Evaluation of the amount of ammonia remaining in the solution was then made by distillation into an excess of acid of known strength and back-titration with sodium hydroxide.

Water.—Horn and Taylor[11] collected the water evolved from the combustion of the ammonates of copper sulfate by absorption in a U-tube containing solid potassium hydroxide. The evolved ammonia passed through the alkali tube and was absorbed in sulfuric acid. An attempt was made to apply this method of determining water and ammonia to the ammonates of copper selenate. It was found that when the temperature was raised to a point required for the complete decomposition of the ammonate, a partial combustion of the ammonia took place. As a result the water results were high and the ammonia low. The explanation for this behavior probably lies in the fact that ammonates of copper selenate de-

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[9] Rivot, *Compt. rend.*, 38,808 (18.54).

[10] Treadwell and Hall, "Analytical Chemistry," Vol II, 1924, 5th ed., p. 186.

[11] Horn and Taylor, *Am. Chem. J.*, 32,253 (1904).

compose principally into copper oxide, selenium dioxide, ammonia and oxygen at 190°. Inasmuch as it is necessary to heat the compounds to at least 180° in order to drive off the last two molecules of ammonia, it is probable that the oxidation takes place when the selenate group decomposes to yield the selenite. Heating in a current of oxygen-free dry nitrogen likewise yielded high water results and low ammonia results.

The method adopted for the determination of water in the ammonates was that of complete combustion in a tube containing copper oxide and metallic copper. Selenium was retained in the boat by covering the sample with a layer of sodium chromate of known water content. The percentage of ammonia having been determined in a separate sample, the water existing as such in the compound was calculated.

Hydrated Ammonates of Copper Selenate

Copper Selenate Tetrammonate Monohydrate.—The method of Dennis and Koller[2] was followed in the preparation of this salt: 100 g. of copper selenate pentahydrate was dissolved in 125 cc. of concentrated ammonia solution and ammonia gas passed into the dark blue solution for two hours. The crystals were filtered on a sintered glass plate, washed with a cold concentrated ammonia solution and desiccated over soda lime for three days. Analysis of the material was in accord with the formula assigned by the above workers.

Anal. Calcd. for $CuSeO_4{\cdot}4NH_3{\cdot}H_2O$: CuO, 27.16; Se, 27.04; NH_3, 23.22; H_2O, 6.15. Found: CuO, 27.04 (av. 3 detns.); Se, 26.91 (av. 4 detns.); NH_3, 22.94 (av. 4 detns.); H_2O, 6.31 (av. 3 detns.).

Ammonia results were usually found to be slightly lower than the calculated values. This was probably brought about as a result of loss of ammonia during the drying process. The color is close to that of Mulliken's standard BV—Shade 2.[12]

Attempts were made to prepare the compound by adding alcohol to ammoniacal solutions of copper selenate. The blue precipitate produced was found to be a basic salt the composition and color of which varied with the preparation. The precipitate corresponded most nearly with the tetrammonate monohydrate when small amounts of alcohol were used in strongly ammoniacal solutions of the selenate.

Copper Selenate Triammonate Monohydrate.—Copper selenate tetrammonate monohydrate when treated with a current of dry air loses one molecule of ammonia to form the triammonate monohydrate. Samples of the tetrammonate were treated in the manner described by Dennis and Koller.[2] Analysis of the product yielded results in harmony with the findings of these workers.

Anal. Calcd. for $CuSeO_4{\cdot}3NH_3{\cdot}H_2O$: CuO, 28.85; Se, 28.72; NH_3, 18.52; H_2O, 6.98. Found: CuO, 28.91; Se, 28.78; NH_3, 18.51; H_2O, 6.90 (all av. of 3 detns.).

The color of this salt is almost identical with that of standard B—Tint I.[12]

The monohydrate of copper selenate under ordinary conditions is the most stable ammonate of the series. The composition of the salt is not altered by prolonged exposure to the air and desiccation over phosphorus pentoxide for several weeks fails to remove the molecule of water. When heated to a temperature of 110° under a pressure of 2 mm. of mercury, water and ammonia are lost. Samples treated in this manner

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[12] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1904, Color Charts, Vol. I.

were found to come to constant weight after a loss of approximately 14%. The calculated loss in weight for the conversion of the triammonate monohydrate to the dihydrate is 12.72%. Analysis of the residue showed that in all cases the amount of ammonia in the material was lower than the calculated amount for the diammonate, the average ammonia content of three typical preparations being 13.65% against a calculated value of 14.14%. Copper and selenium results were correspondingly high.

Copper Selenate **Tetrammonate Dihydrate.**—Willy Lange[3] has reported the isolation of an ammonate of the composition $CuSeO_4 \cdot 4NH_3 \cdot 2H_2O$. The only analysis reported upon the compound is one water determination which is about 1% lower than the calculated value. The compound is described as a very easily soluble, sky-blue crystalline substance which by the loss of water yields the blue-violet anhydrous tetrammonate.

Various methods were used in an effort to isolate this compound. Ammonia gas when passed into either dilute or concentrated solutions of copper selenate always yielded the monohydrate. It had been previously noticed that by cooling the reaction tube during the precipitation of the tetrammonate monohydrate, an increased yield of the product was obtained. It was thought that the greatly lessened solubility might indicate that the dihydrate was the stable phase at temperatures in the neighborhood of 0° and that during subsequent operations decomposition took place with the formation of the monohydrate. Accordingly an effort was made to isolate and dry the product at a temperature but slightly above 0°. Precipitation of the salt was brought about by passing ammonia gas into a solution of copper selenate contained in a pyrex test-tube. The tube was immersed in an ice–salt mixture at a temperature of about −2° at the time of precipitation. It is interesting to note that the deposition of the ammonate from solution is nearly complete at this temperature, the supernatant liquid having but a faint blue color after crystallization. The precipitate was quickly transferred to a sintered glass filter provided with a jacket through which cold brine was circulated. The blue material was washed several times with a solution prepared by saturating water with ammonia gas at 0°, transferred to a soda lime desiccator and placed in the lower compartment of an electric refrigerator. At no time did the temperature of the product greatly exceed 4°.

Analysis of several products so prepared did not yield results in agreement with the calculated values for the dihydrate. In order to safeguard against possible loss of appreciable amounts of ammonia or water during the weighing process, large samples were taken from previously weighed glass stoppered bottles, quickly transferred to dilute acid solutions and diluted to known volumes. Analysis of aliquot portions enabled us to determine the percentages of the various constituents in the original sample. Water thus determined by difference was usually high by one or two per cent. In no case did the complete analysis agree with the calculated values for the dihydrate.

Because of our inability to isolate the dihydrate with the aid of ordinary precautions, it was thought advisable to investigate the warming curve of the compound formed by the action of ammonia gas on a solution of copper selenate at 0°. Accordingly a large quantity of the ammonate was precipitated at −1° and isolated in the usual manner. When the deposition of the product was complete the supernatant liquid was removed and the ammonia inlet tube replaced by a thermometer. The ammonia gas was swept from the tube by means of a blast of air and the sample quickly mixed with about one-third its volume of cold copper selenate tetrammonate monohydrate of established purity. The reaction tube, which throughout this manipulation was cooled in brine, was wrapped in several thicknesses of cold cloth and allowed to warm slowly. Examination of one of the characteristic curves obtained in this manner (Fig. 1) shows the absence of the break which usually accompanies a change of the solid phase. Temperature readings were taken every thirty seconds and the total time of the experiments was about forty-five minutes. It is to be concluded as a result of the physical and chemical investigation either that the compound described by Lange does not exist or that it is not formed under the conditions described in the above experiments. The product obtained by Lange was in all probability the tetrammonate monohydrate which contained water mechanically retained in the crystals. It has been noted that the monohydrate is dried with difficulty.

Anhydrous Ammonates of Copper Selenate

Copper Selenate **Pentammonate.**—Copper selenate pentahydrate when exposed to ammonia gas behaves in much the same manner as the corresponding hydrate of copper sulfate.[13] Copper selenate pentahydrate when exposed to a stream of ammonia gas very quickly evolves heat, turns dark blue and assumes a pasty consistency. The tetrammonate monohydrate behaves in a similar manner. Prolonged exposure of either of the two salts to anhydrous ammonia under a pressure of 10 cm. of mercury and at a temperature of 0° results in a quantitative absorption of ammonia to produce the pentammonate of copper selenate, a dark blue product which upon warming evolves ammonia and which very quickly decomposes in moist air. The pentammonate may be prepared most conveniently by the action of liquid ammonia on copper selenate tetrammonate. The monohydrate is first treated with a slow stream of anhydrous ammonia gas at slightly elevated temperatures in order to remove the water. The resulting product is transferred to a pyrex test-tube and immersed in a Dewar flask containing liquid ammonia. Liquid ammonia is then condensed in the reaction chamber. The low temperature and the pressure are sufficient completely to transform the tetrammonate to the pentammonate. Samples of the product after removal of the excess liquid ammonia were sealed in small tubes, weighed and broken under dilute hydrochloric acid. Analysis for various constituents was then made on the filtrate in the usual manner.

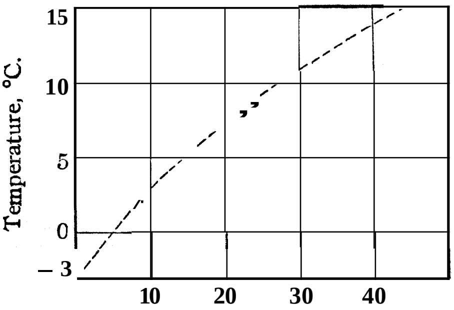

Fig. 1.

Anal. Calcd. for $CuSeO_4 \cdot 5NH_3$: CuO, 27.22; Se, 27.13; NH_3, 29.25. Found: CuO, 27.01; Se, 27.05; NH_3, 29.12 (all av. of 4 detns.).

The transition point for the system copper selenate pentammonate–copper selenate tetrammonate was determined dilatometrically to be at 19 ± 0.3°. The color of the pentammonate is between that of the standards B and BV of the normal tones.[12]

Kao[6] found from a study of the copper selenate–water system evidence which led him to suspect strongly the existence of a heptahydrate of copper selenate at low temperatures. Attempts to isolate the heptammonate of copper selenate have failed. Chemical analysis of the product formed by the action of liquid ammonia on copper selenate, copper selenate pentammonate and copper selenate tetrammonate yielded results which were not concordant with different preparations and which did not correspond to those calculated for any one simple compound. Inasmuch as Ephraim[14] has shown that in some cases of this type a continuous series of solid solutions exists between different ammonates and ammonia, it is doubtful if analytical results would have great

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[13] Horn, *Am. Chem. J.*, 39, 195 (1908).

[14] Ephraim, *Ber.*, 52, 940 (1919).

significance anyhow. Investigation of the warming curve of the copper selenate–ammonia system between the temperature of boiling liquid ammonia and 15" yielded no irregularity which might be attributed to compound decomposition. It is to be concluded that if the pentammonate of copper selenate does exist it is not stable at atmospheric pressure above the boiling point of liquid ammonia.

Copper Selenate Tetrammonate.—This compound has been previously reported by Dennis and Koller[2] and more recently by Willy Lange.[3] The former investigators obtained the product as a result of the decomposition of copper selenate tetrammonate monohydrate at room temperature under a pressure of 27 mm. of mercury and in the presence of freshly ignited quicklime. Lange gives none of the details of preparation but states that the compound is formed as a result of the decomposition of the tetrammonate dihydrate with the production of the anhydrous product.

The directions of Dennis and Koller were followed in the preparation of this compound. After seven days in a desiccator containing lime and at a pressure of about 17 mm. of mercury it was found that the tetrammonate monohydrate had lost water and that there was formed the anhydrous tetrammonate. Analysis of representative samples yielded results substantially in agreement with those calculated from the assigned formula.

Anal. Calcd. for $CuSeO_4 \cdot 4NH_3$: CuO, 28.94; Se, 28.84; NH_3, 24.76. Found: CuO, 28.41; Se, 28.81; NH_3, 24.94 (av. of 4 detns.).

The tetrammonate is stable above 100" provided the sample is maintained in an atmosphere of ammonia gas. Because preparations made according to the method of Dennis and Koller usually appeared to have undergone a secondary decomposition with the production of a small amount of the triammonate monohydrate and basic salts, the following method of preparation was devised to yield a product free from the triammonate monohydrate.

Copper selenate pentahydrate of established purity was dissolved in water and 50 cc. of the saturated solution transferred to a large pyrex test-tube fitted with a delivery and outlet tubes. Ammonia gas was passed into the hot solution and after most of the water had been removed the tube was transferred to an oil thermostat regulated to about 120°. Passage of the ammonia was continued through the blue mass until the last traces of water had been removed. The preparation was removed, crushed and again treated with ammonia gas at 120°. Analysis of several products prepared in this manner yielded results in strict agreement with the calculated values. In two typical preparations the ammonia content was found to be 24 70 and 24.76% against the calculated value of 24.76%. The color of the tetrammonate is between that of standards VB and BV of the normal tones.[12]

Copper Selenate Diammonate.—Horn and Taylor[11] prepared a series of apple-green decomposition products of copper sulfate tetrammonate and concluded that the products were basic salts and not definite chemical individuals. Lange[3] has reported that if heated the tetrammonate of copper selenate will pass directly without melting to the diammonate.

It was found that if the anhydrous tetrammonate of copper selenate was heated with access to air there were formed various decomposition products, the ammonia content of which was usually lower than that calculated from the diammonate and which varied depending upon the length and rapidity of heating as well as with the maximum temperature. Samples of the tetrammonate placed in an oven regulated at 80° lost approximately 12.5% in weight. Although this loss corresponds rather closely to the calculated loss in the conversion of tetrammonate to the diammonate, the analytical results were not in close agreement for the calculated values for the diammonate. If. however, the sample is maintained in an atmosphere of ammonia gas at atmospheric pressure, the loss in weight will not be appreciable until the temperature of 178" is reached. At this point ±2° the compound breaks down to form the diammonate. Analyses of the products obtained by heating copper selenate tetrammonate to a temperature of 185° in an atmosphere of ammonia gas at atmospheric pressure are in close agreement with the calculated values.

Anal. Calcd. for $CuSeO_4 \cdot 2NH_3$: CuO, 33.04; Se, 32.88; NH_3, 14.14. Found: CuO, 33.03; Se, 32.56; NH_3, 14.14 (all av. of 3 detns.).

The diammonate is a light blue powder. It corresponds somewhat to the BG normal tone of Mulliken's standards[12] and is insoluble in water but soluble in dilute mineral acids and ammonia solution. The compound is stable if preserved in a closed container. Below 178° the material absorbs ammonia to form either the tetrammonate or the pentammonate depending upon the temperature and pressure. Heated above 192' the diammonate is decomposed with the production of ammonia and a black residue which consists of a mixture of copper oxide and copper selenide. Selenium dioxide has been noticed in the cooler parts of the reaction tube when the temperature exceeds 200".

Summary

1. Copper selenate pentammonate and copper selenate diammonate have been prepared and identified.
2. A new and satisfactory method for the preparation of copper selenate tetrammonate has been described.
3. No evidence was found for the existence of the tetrammonate dihydrate of copper selenate reported by Lange.
4. Copper selenate tetrammonate monohydrate, copper selenate tetraammonate and copper selenate triammonate monohydrate have been prepared according to the methods of Dennis and Koller. Analysis of the products indicates composition in accord with ascribed formulas.

MADISON, WISCONSIN

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

MOLECULAR RAY EXPERIMENTS. THE CHEMICAL ACTIVITY OF MOLECULAR AND ATOMIC OXYGEN[1] .

BY WORTH H. RODEBUSH AND W. A. NICHOLS, JR.

RECEIVED JUNE 23, 1930 PUBLISHED OCTOBER 6, 1930

The initial purpose of this investigation was to find some chemical reaction by which the image of a beam of oxygen molecules could be formed on a target for a Stern–Gerlach experiment. The first attempts in this direction in this Laboratory were made at the time that the magnetic moment of atomic hydrogen was measured. It became evident[1c,d] at that

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[1] Previous publications on molecular rays from this Laboratory are as follows: (a) Kunz, Taylor and Rodebush, *Science*, 63, 550 (1926); (b) Taylor, *Phys. Rev.*, 28, 576 (1926); (c) Phipps and Taylor, *Science*. 64, 480 (1926); (d) Phipps and Taylor, *Phys. Rev.*, *29*, 309 (1927); (e) Rodebush, *Proc. Nat. Acad. Sci.*, *13*, 50 (1927); (f) Rodebush and Copley, *Phys.* Rev., 33, 1083 (1929); (g) Kurt and Phipps, *ibid.*, 34, 1357 (1929); (h) Rodebush and Nichols, *ibid.*, 35, 649 (1930); (i) Shaw, Phipps and Rodebush, *ibid.*, 35, 1126 (1930).

time that there were certain interesting chemical problems in connection with the reactions of molecular rays and that, furthermore, molecular rays constitute an especially powerful method of studying heterogeneous reactions because it is possible with an inhomogeneous magnetic field to determine not only the molecular species that is reacting but the actual state of excitation as expressed by the spectroscopic term. For instance, the only absolute test for atomic hydrogen is the Stern–Gerlach experiment. The main purpose of this paper has been the investigation of the chemical activity of the various molecular species that can be produced in oxygen.

Molecular Oxygen.—Molecular oxygen reacts readily with the polished surfaces of certain metals, *e.* g., copper, at slightly elevated temperatures and the film of oxide formed is readily visible One interesting question which arises at once is: will the reaction take place between a beam of cold molecules and a hot surface or between a beam of hot molecules and a cold surface? In this connection it should be noted that the average temperature of a molecule beam is higher than the temperature of the gas in front of the source slit. The average kinetic energy normal to the surface of the molecules striking a surface is kT. If we interpose a slit system we select only the faster molecules, so that the average kinetic energy in the direction of the beam is now $2kT$. This process of selection lowers the effective pressure of the beam enormously, so that it is difficult to obtain beams with effective pressures greater than 10^{-6} mm. This pressure is often considerably less than the pressure obtainable with the best pumping conditions in the apparatus beyond the slit system and constitutes a serious limitation to the chemical activity.

The reactivities of cold surfaces of metallic silver, copper and sodium, phosphorus, indigo and a number of lower oxides, including those of lead and molybdenum, were tried without any observed result. In a number of trials the oxygen molecules were heated to temperatures of several hundred degrees centigrade. No reaction was observed in any case. It was thought that the oxide film might be difficult to observe and a copper target which had been exposed to a beam of oxygen molecules was exposed to mercury vapor. If a similar experiment is made with electrons, the spot which has been bombarded does not amalgamate[2] but complete amalgamation was always obtained with targets bombarded by oxygen molecules. It seems probable that the temperature of the surface itself must be raised in order to bring about a reaction with oxygen molecules. The part played by water in oxidation must not be overlooked. In the high vacuum the surfaces must be very dry and it is well known that in the case of sodium, for example, the presence of moisture catalyzes the oxidation of the surfaces. It could be predicted in advance that no reaction would be obtained between a beam of oxygen molecules and a hot copper

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[2] Carr, *Phys. Rev.*, 33, 1068 (1929).

or silver surface because the dissociation pressure of the oxide is greater than the partial pressure of oxygen in the beam.

Atomic Oxygen.—Langmuir's[3] method of thermal dissociation was tried. An iridium filament was used at first. Iridium has a high melting point and its oxide is reported to dissociate at high temperatures, so that furnaces wound with iridium wire can be operated in contact with the atmosphere. At low pressures of oxygen, however, the glass walls near the filament were soon coated with a black deposit of what was presumably iridium oxide so that the use of iridium was abandoned in favor of platinum. With a platinum filament heated near its melting point in an oxygen pressure of a few tenths of a millimeter marked oxidizing action was obtained on a large number of substances which were introduced into the chamber within a few centimeters of the filament. It was not possible to say whether the active species was atoms or activated molecules, and it was not possible to obtain any activation in a beam formed with the hot filament directly in front of the source slit. The lack of activity in the beam is probably accounted for by the very small concentration of active species existing in the neighborhood of the filament.

In all further experiments upon atomic oxygen the electrodeless discharge was used. This arrangement eliminates the disturbing action of the electrodes and the frequent replacement of electrodes necessary with a gas such as oxygen. Details of such an apparatus have been described by Kurt and Phipps.[1g]

The reaction of oxygen in the electrodeless discharge at a partial pressure of 0.1 mm. is strongly oxidizing upon any substance placed in the discharge tube. Lead oxide is oxidized to the dioxide, the blue reduced oxide of molybdenum is converted to the yellow trioxide and numerous other substances were tested in a similar way. No exceptions were found to this generalization and the reaction was extremely rapid.

Reducing Action of Atomic Oxygen.—The only reaction hitherto recorded for molecular beams from the oxygen discharge is the conversion of lead oxide to the dioxide, which was used by Kurt and Phipps. They showed by the magnetic moment that this reaction was due to the atom.

It is well known in chemistry that molecular oxygen is evolved by hydrogen peroxide in the presence of many metallic oxides and the reaction is usually described as reduction. A satisfactory mechanism is provided if it is assumed that the hydrogen peroxide liberates atomic oxygen. This suggested to the authors that a similar reducing action might be anticipated with atomic oxygen. Silver oxide was tried first and afterward a number of other metallic oxides, including the trioxides of tungsten and molybdenum. A surface coated with the oxide was exposed to the beam from the electrodeless discharge in oxygen for some hours. The beam was formed by two

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[3] Langmuir, THIS JOURNAL, 37, 417 (1915).

slits 0.1 mm. in width by 1.4 mm. length placed six cm. apart. No reaction was obtained with any oxide except molybdenum trioxide. In the case of molybdenum trioxide a slate-blue image was produced on the target which appeared like the image produced by atomic hydrogen. The slate blue color is generally accepted as characteristic of one of the lower oxides of molybdenum, probably Mo_3O_8. The image could be obtained with atomic hydrogen in about fifteen minutes. With atomic oxygen a somewhat longer time was required but the image always appeared in less than an hour.

Pure oxygen was prepared from various sources and passed over heated copper oxide to remove traces of hydrogen. The oxygen was always passed through a liquid-air trap. In every case the reaction was obtained, so that it was shown conclusively that the reaction was produced by pure oxygen containing only the traces of water vapor that might be given off by the walls of the discharge bulb. As the discharge bulb was often operated continuously for hours and in some cases a second liquid-air trap was connected directly to the discharge bulb, the amount of moisture in the oxygen must have been very small indeed in some runs, but the reaction was not noticeably affected. Copeland[4] has reported that an appreciable amount of water vapor must be present in order to obtain a good line spectrum with the electrodeless discharge in oxygen. We are not able to confirm this. The discharge was not quite so steady when the second liquid-air trap was connected directly to the bulb but in all cases the line spectrum of oxygen was obtained and the reaction with the trioxide. It is our opinion that water vapor is not necessary to bring about the dissociation of oxygen, but that its presence is necessary to prevent the recombination of the atoms on the walls of the tube is shown conclusively by the work of Rodebush and Troxel on the heat of dissociation.[5]

The molybdenum trioxide was "smoked" on the target in a finely divided condition by burning a molybdenum wire under it. It was not possible to produce enough of the "reduced" oxide to make any sort of a chemical analysis but when beams of atomic oxygen and atomic hydrogen were alternately impinged on the target no change in the appearance of the blue image was observed. It was not possible to produce the blue coloration with atomic oxygen unless the target was separated from the discharge tube by two slits. When a single pinhole slit was used, no action was obtained on the target.

In order to identify the active species the oxygen beam was passed through an inhomogeneous magnetic field using the arrangement described by Kurt and Phipps. The central undeviated line was obtained but the fainter side lines characteristic of atomic oxygen were not obtained although the run was continued for more than twenty-four hours.

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[4] Private communication to the authors.

[5] To be published shortly.

The reaction which takes place between a beam of atomic oxygen and molybdenum trioxide is believed to be

$$3MoO_3 + O = Mo_3O_8 + O_2$$

It has not been proved of course that the reaction is the same for atomic oxygen as for atomic hydrogen. It seems very doubtful, however, if a higher oxide of molybdenum than MoO_3 would have an appearance identical with the partially reduced oxide and none is known to exist. This conclusion is strengthened by the fact that the blue oxide is quickly changed to the yellow trioxide on direct contact with the discharge in oxygen, which has been shown to have a strongly oxidizing action on most substances.

The Stern-Gerlach experiment shows that the reducing action cannot be due to *hydrogen,* traces of which might be produced from the water evolved from the glass surfaces. Since the side lines characteristic of the oxygen atom were not obtained, it does not prove conclusively that atomic oxygen is the reducing agent. The central undeviated line might be due to the OH molecule or to an activated oxygen molecule in the $^1\Sigma$ state for example. Since the hydroxyl molecule must be present in vanishingly small amounts and it is difficult to formulate a reaction for either hydroxyl or the oxygen molecule, there seems to be no reason to doubt that the reaction is due to the oxygen atoms.

There remains to be considered the question of why the side lines were not obtained in the Stern-Gerlach experiment. These side lines are characteristic of the $^3P_1$ and $^3P_2$ states of the oxygen atom. It might be assumed that only the $^3P_0$ state reacts with the molybdenum trioxide but this would appear a fanciful hypothesis. The more reasonable explanation is to be found in the fact that the reduction can only be brought about when the active species is passed through a double slit system. Evidently the reducing action can only take place in the presence of a very low pressure of molecular oxygen. The partial pressure in the deflected beam of the atoms in the $^3P_1$ and $^3P_2$ states is very small indeed and we may suspect that there is a critical value for the ratio of the partial pressure of atoms to the partial pressure of molecules below which the reduction does not take place.

Summary

An exhaustive search failed to discover any surface with which a beam of oxygen molecules will react to give a visible image.

A beam of oxygen atoms appears to give the same reaction with molybdenum trioxide as a beam of atomic hydrogen. This reaction is believed to be represented by the equation

$$3MoO_3 + O = Mo_3O_8 + O_2$$

URBANA, ILLINOIS

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE. IN COOPERATION WITH THE UNIVERSITY OF CALIFORNIA]

THE VAPOR PRESSURE OF ANTIMONY TRIOXIDE[1]

BY W. B. HINCKE[2]

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During the past few years the Pacific Experiment Station of the U. S. Bureau of Mines has received many inquiries regarding the vapor pressure of antimony trioxide. The applicability of such information to the study and improvement of technical methods involved in lead softening, as well as the possible value of such data to the manufacturer of pigments and rubber fillers, has been the incentive in making the following measurements. This work also has an essential place in a general program of investigation being carried on by the Pacific Experiment Station of the Bureau, dealing with the determination of the thermodynamic properties of metallurgically important materials, such as oxides and sulfides.

Preliminary Measurements and Selection of Methods.—Solid antimony trioxide exists in two crystalline forms, cubic and' orthorhombic, and has a transition temperature at 570 ± 10° as determined by Roberts and Fenwick.[3] The cubic form is stable below the transition temperature, and the orthorhombic modification is stable from the transition temperature to the melting point, which has been given by Quercigh[4] as 656°. Preliminary experiments showed that vapor pressures ranging from a fraction of a millimeter to a total of several centimeters prevail in the temperature range 500–800°.

Two serious difficulties beset any attempt to measure vapor pressures of antimony trioxide. At very low total pressures, thermal dissociation of the oxide becomes apparent, and in fact it proved impossible to resublime even under moderate vacua without always producing small amounts of antimony metal. At higher temperatures, and especially in the case of the molten oxide, the material is an active slagging as well as oxidizing agent, preventing the extensive use of both vitreous and metallic containers.

After some testing of a variety of materials, silica glass was found usable below about 800°, when the time of contact of liquid oxide and glass was not too great, although it was slowly and continuously slagged.

From these preliminary experiments it was apparent that the inert gas saturation method would be suitable for the determination of the vapor

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Assistant Physical Chemist, Pacific Experiment Station. U. S. Bureau of Mines, Berkeley, California.

[3] Roberts and Fenwick, THIS JOURNAL, 50, 2125 (1928).

[4] Quercigh, *Atti Accad. Lincei,* [5] 21,415 (1912).

pressures of the solid oxide, but that ordinary methods such as the "boiling point" method would be unsuitable for the liquid, both because of the order of magnitude of pressure involved, and because long contact and agitation were to be avoided to prevent excessive slagging. By the use of a special form of tensimeter the difficulties attendant upon measurements of the liquid oxide were overcome in sufficient degree to furnish adequate, if not completely satisfactory, vapor pressures. Experiments upon the solid oxide, by the inert gas method, and upon the liquid by the new method, will be described separately, and in order.

Part I. Sublimation Pressures of Solid Antimony Trioxide

Preparation of Materials.—Samples of cubic and orthorhombic crystals were prepared by repeated sublimation and condensation in vacuum, and finally in nitrogen, at a temperature at which only the desired crystalline form was stable. Since antimony trioxide readily absorbs oxygen at elevated temperatures, to give more stable higher oxides (tetroxide), great care was taken to prevent the presence of elemental oxygen both during preparation and measurement.

Method.—The inert gas saturation method used for the solid forms of oxide was practically identical with that used by Eastman and Duschak[5] and need not be again described. One essential modification which was made, however, consisted in the fitting of the apparatus with a condenser tube of very light mass (about 1 mm. bore) which could be weighed on the button balance. Experiments of long duration were unsatisfactory because of the slight corrosive action of antimony trioxide vapor on the weighing tube even at a few millimeters' partial pressure. It was better, therefore, to use a sensitive button balance to determine a few milligrams of condensed oxide rather than to attempt to secure equal accuracy from greater amounts of condensed oxide produced over longer sublimation periods.

The lower limit of pressures measurable by the saturation method was determined by the precision with which minute quantities of sublimate deposited in the gas outlet tube could be weighed. All other factors, such as the completeness of saturation and the accuracy of measurement of the volume of nitrogen and the temperature of the furnace, were so controlled as to produce negligible errors in comparison with the unavoidable variations of weights. By the use of the button balance the limit of the vapor pressure measurements was extended to a low range; in fact, weighings were made of samples of condensate as small as 0.00016 g., corresponding at 460° to a partial pressure of 0.0169 mm. of antimony trioxide vapor in the saturator.

At temperatures above 600° the corrosive action of the antimony trioxide vapor began to glaze the inside surface of the quartz saturation chamber as well as to attack the quartz outlet tube with considerable effect on the accuracy of weighing the deposited sample. This glazing action, although not completely disastrous to the method up to 640°, may account for the slight irregularity of the values in this range (see Fig. 2).

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[5] Eastman and Duschak, U. S. Bureau of Mines Technical Paper 225.

Results of Inert Gas Method.—In Table I are shown the results obtained by measurements on cubic crystals of antimony trioxide, and Table II shows similar figures for the orthorhombic form. In the calculation of vapor pressures, the mole of trioxide in the gas phase was taken as Sb_4O_6, in accordance with the results of V. Meyer and H. Mensching[6] and of Biltz.[7] The pressures are reduced to millimeters of mercury at 0°.

The determined values in Tables I and II are shown as individual points in the chart of Fig. 2, where the logarithm of pressure is plotted against the reciprocal temperature in the conventional way.

TABLE I

VAPOR PRESSURE BY INERT GAS METHOD OF CUBIC CRYSTALS

Temp., °K.	Mole of N_2 (satd)	Weight of Sb_2O_3 condensed, g.	Total press., mm. of Hg	Calcd. press. $(Sb_2O_3)_2$, mm. of Hg	Log p, (mm.)	$\frac{10^6}{T. °K.}$
742	0.01227	0.00016	758.4	0.0169	−1.7705	1348
755	.01543	.00038	758.2	.0319	−1.4955	1325
767	.01561	.00064	754.8	.0528	−1.2783	1305
780	.01676	,00104	754.0	.0802	−1.1060	1285
797	.01400	.00165	759.9	.1530	−0.8145	1255
816	.01423	.00350	759.3	.319	− .496	1226
827	.00917	.00358	757.3	.505	− .296	1210
839	,01041	.00566	756.1	.703	− .153	1191

TABLE II

VAPOR PRESSURE BY INERT GAS METHODS OF ORTHORHOMBIC CRYSTALS

Temp., °K.	Mole of N_2 (satd)	Weight of Sb_2O_3 condensed, g.	Total press., mm. of Hg	Calcd. press. $(Sb_2O_3)_2$, mm. of Hg	Log p, mm.	$\frac{10^6}{T, °K.}$
742	0.01148	0.00019	758.9	0.0215	−1.668	1348
742	.01237	.00020	763.5	0.02108	−1.676	1348
862	.01625	.0198	762.8	1.585	0.205	1161
862	.01596	.0196	761.4	1.594	.203	1161
862	.01717	.0210	760.1	1.580	.199	1161
876	.01634	.0278	759.8	2.200	.343	1141
876	.01626	.0263	759.7	2.095	.322	1141
888	.01530	.0393	762.0	3.330	.523	1126
886	.01616	.0399	760.9	3.231	.509	1126
897	.01740	.0599	761.7	4.470	.651	1114
900	.01537	.0428	759.1	3.600	.557	1110
900	.01507	.0485	759.6	4.155	.619	1110
917	.01580	.0735	758.0	5.980	.777	1090

Part II. Vapor Pressures of Liquid Sb_2O_3

Method.—The tensimeter method used for liquid oxide is best described by reference to the diagram of Fig. 1. A U-manometer of silica glass, M, has parallel legs five or six inches long, axially separated some four inches. Each leg is provided with a silica glass hook, H, one of which engages the fixed support R, the other being connected

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[6] V. Meyer and H. Mensching, Ber., 12, 1282 (1879).

[7] H. Biltz, *Z. physik. Chem.*, 19, 385 (1896).

through the quartz glass fiber *G* with the arm of a good analytical balance, B. The whole manometer is thus freely suspended in the uniform temperature zone of an electric furnace, F. The leg at the fixed support has the side arm S, containing the oxide to be measured. The manometric fluid B is metallic bismuth. Both legs of the manometer are highly evacuated at the beginning of an experiment, and sealed, the temperature of the whole being below that at which vapor pressure is detectable. When the whole manometer is now slowly heated, the displacement of the bismuth column due to vaporization of oxide is determinable from the weight necessary to restore the zero position of the balance.

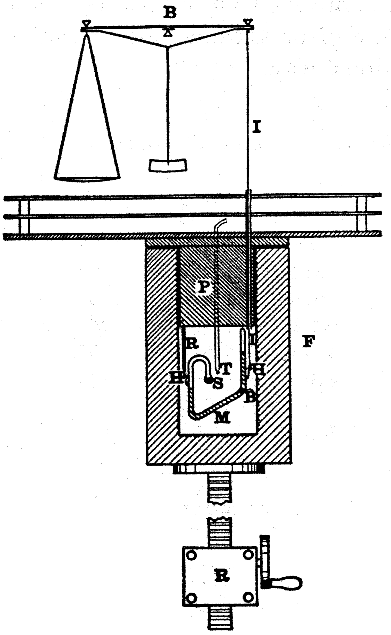

Fig. 1.

The manometer swings freely between the supports and finds its equilibrium position. It is obvious that the center of gravity must be so adjusted that the two legs of the manometer remain stable in the vertical plane, but the center of gravity must not be too far below the axis of support if good sensitivity is to be obtained.

The balance B is well shielded from the heat of the furnace, the quartz fiber connection being made through a small-bore silica glass tube inserted in the insulating material and plug P. The top of the furnace and the balance are rigidly mounted by suitable supports. The furnace itself is cylindrical in shape with inside dimensions 5 × 14 inches. It is mounted on a geared rack and may be raised about the manometer and fitted snugly about the top plug P.

It is apparent that this tensimeter must be calibrated before use. The balance weighings give in effect only the displacement of the center of gravity of the instrument as produced by the shift of the manometer liquid. The calibration is accomplished by determining the change in apparent weight produced by known heights of mercury in the cold manometer.

The manometer tubes were selected for uniform bore, and so formed that the two arms were parallel and straight over the height of column to be used. For the purpose of calibration the ends were left unsealed and were about half filled with clean mercury. A small Bunsen valve was fitted on the high side of the manometer in order that the mercury might be held at various levels during the calibration. The furnace F was lowered and the manometer with the mercury was suspended so that the high side hung from the quartz fiber. The supports were so adjusted that the center of gravity was well up near the line between the two supports, but low enough so that the manometer was always stable in the vertical plane, when the difference in columns was a maximum. When the manometer is held in the zero position, as indicated by the pointer of the balance, only vertical forces are transmitted by the fiber suspension.

For the actual calibration a cathetometer was used to make readings of the heights of the various displacements of the mercury column corresponding to the weights balancing the downward force on the quartz fiber. Figure 3 shows a graph of such weighings in grams and corresponding heights in centimeters of mercury, and constitutes a calibration for one of the manometers used. If the manometer were perfectly constructed and the suspension were frictionless and unaltered during the calibration, the points would fall on a straight line. Each manometer had its own characteristic curve, but the slope of the line depends only upon the bore of the tube and the distance between the two supports. The nearly precisely constant ratio between increases in weight and increases in pressure over the whole range of the manometer is shown in Fig. 3, by the close approximation to a straight line. The chart shows that an increase in 1 g. weight of the downward force on the quartz fiber support corresponds to an increase of 0.5823 mm. of mercury pressure in the manometer. Since silica glass has little thermal expansion, the calibration of the apparatus remains practically unaltered over wide temperature ranges. Moreover, it is obvious that for any other manometer fluid of different density ranging over the same heights of column for which the calibration

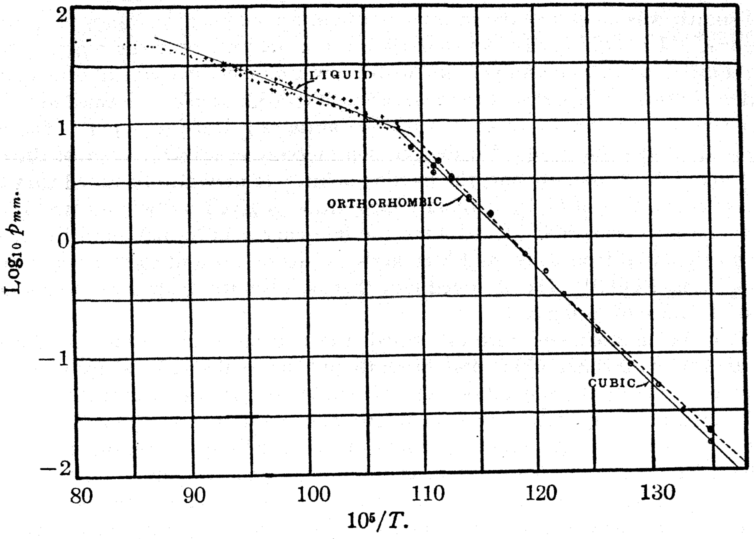

Fig. 2.

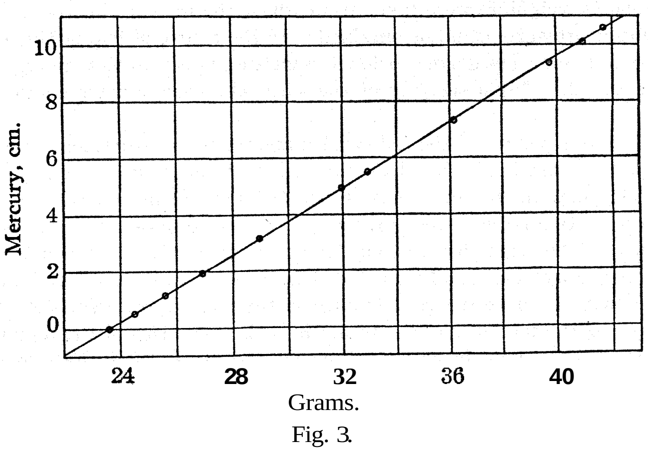

Fig. 3.

was made, the increment of weight above that corresponding to zero pressure will always be proportional to the pressure (measured in mm. of mercury) as determined from the calibration chart with mercury, provided that the bore of the manometer is true to within the accuracy of weighing. This avoidance of density corrections for the manometer fluid at high temperatures is one of the chief advantages of the tensimeter.

Bismuth was chosen as the manometric fluid for making the vapor pressure determinations. It is liquid and has a negligible vapor pressure over the range of temperatures required, and has no stable oxide with a lower dissociation pressure than antimony trioxide. If this latter were not the case bismuth trioxide would be formed in the sample side of the manometer by reaction with the antimony trioxide vapor. The work of Simon and Thaler[8] has shown the dissociation pressure of $(Sb_2O_3)_2$ to be of the order of magnitude of 10^{-8} mm. at 656°, the melting point. It may also be noted that the free energy of formation of Sb_2O_3 at room temperature as given by Schuhmann[9] is -148.6 Cal., which is considerably greater than the free energy of formation of Bi_2O_3, -119.2 Cal., as calculated from Ditte and Metzner's[10] value of ΔH and the known entropies of Bi,[11] O_2[12] and Bi_2O_3.[11] The observed fact that no bismuth oxide was formed confirms the initial choice of bismuth.

After the manometers were calibrated, the two open ends were sealed onto two silica glass tubes through which pure bismuth and the solid sample of antimony trioxide were introduced into the apparatus. It was found to be very important that both sample and bismuth be completely outgassed before sealing the manometer and again pulling off the evacuating tubes. This was practically accomplished by heating the bismuth to a red heat for a considerable time while maintaining a good vacuum on both sides of the manometer. Finally the sample of antimony trioxide was fused in the small bulb S and the manometer sealed off and disconnected from the evacuating apparatus.

The outgassed and sealed tensimeter was now ready to suspend in the furnace. The furnace was brought up to temperature beforehand so that the danger of the bismuth freezing and breaking the manometer was avoided. At the outset the temperature was such that a weighing corresponding to a negligible pressure of $(Sb_2O_3)_2$ could be determined. The temperature of the furnace was then gradually increased and at regular intervals weighings were taken from which the increase in weight and the corresponding vapor pressures could be obtained. In the course of two or three hours a temperature range from a few degrees below the melting point up to temperatures of about 800° was covered. Rapid slagging of the silica glass manometer commenced at this point.

To check the results of the balanced manometer, measurements were also made with a stationary tensimeter in which the height of the manometer columns was read directly. This manometer was similar to the balanced form, but was fixed in a special furnace made of two large electric muffle heaters placed about 2.5 cm. apart in a well-insulated box. The silica glass manometer was in the middle uniform temperature region between the two plates. Bismuth was again used as manometer liquid. Narrow slits covered with clear mica were left open in the two opposite ends of the furnace in order to observe the meniscus of the bismuth in the two arms of the manometer. The lighting of the inside of the furnace was through the slot in the furnace opposite to that through which the cathetometer was sighted. The side of the manometer containing the sample of antimony trioxide was evacuated and sealed. The arm into which the

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[8] Simon and Thaler, *Z. anorg. Chem.*, **162**, 253 (1927).

[9] Schuhmann. THIS JOURNAL, **46**, 59 (1924).

[10] Ditte and Metzner, *Compt. rend*, **115**, 1303 11892).

[11] Anderson, THIS JOURNAL, **52**, 2720 (1930).

[12] Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

liquid bismuth was displaced was kept connected to an evacuating system during the measurements. The pressures were determined by reading the height of the bismuth column directly with a cathetometer.

In using the stationary tensimeter, corrections for the density of the liquid bismuth at various temperatures are necessary. The data for this were taken from the work of Yoscharu and Maleyama.[13]

Results of Measurements on Liquid Oxide

The method of the balanced manometer furnishes a large number of experimental observations at temperatures differing by small intervals, and it would seem unnecessary to present data for all individual points. Figure 2 shows the individual points obtained. The results of the balanced nanometer method are shown as dots and the direct readings as crosses.

The determinations by the balanced manometer method were made on a single sample of oxide with the manometer for which the calibration curve is shown in Fig. 3. Two complete series of determinations were made over the temperature range from 600 to 800°. In a third final series the temperatures were carried to the slagging point of the sample, evidenced by a noticeable vapor-pressure lowering. This occurred at about 800°, as is clearly shown by the falling off of the plotted values at the high temperature end of the liquid-phase curve of Fig. 2. The last series was stopped at 975°, and at this temperature the contamination of the sample with slagged silica was such that there was no further vapor-pressure increase with temperature rise. There exists a range of about 150° over which the vapor pressures of the liquid phase were satisfactorily measurable. Because of the extremely corrosive nature of liquid antimony trioxide and its power to react with materials suitable for apparatus construction, it is doubtful whether the range could be lengthened.

The results obtained with the stationary manometer, shown as crosses in Fig. 2, are in fair agreement with those obtained by the balanced manometer method. Two series of determinations on a single sample were made over a temperature range from 650 to 800°. The first series was made on slowly ascending and the second on a descending temperature–pressure scale. At the completion of the measurements the sample of antimony trioxide solidified crystalline, but analysis showed a molal content of 10% of silica. This large content of silica in the sample may have been partly due to a thin shell of quartz glazed with antimony trioxide which scaled off the inside of the manometer on removing the mass of solidified sample.

Derived Vapor Pressure Data.—Assuming that the data obtained may be expressed by a straight line upon a log p–$1/T$ chart, analytic expressions may be obtained for the various forms of oxide. The vapor pressure of

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[13] Yoscharu and Maleyama, *Sci. Refits. Tôhoku, Imp. Univ. 1st series,* *18,* 19–46 (1929).

cubic antimony trioxide as shown in the corresponding curve of Fig. **2** is

$$\log_{10} p_{\text{mm.}} = 12.195 - \frac{10{,}357}{T}$$

that for orthorhombic,

$$\log_{10} p_{\text{mm.}} = 11.318 - \frac{9625}{T}$$

and for the liquid

$$\log_{10} p_{\text{mm.}} = 5.137 - \frac{3900}{T}$$

where log p is the common logarithm of vapor pressure expressed in millimeters and T is the absolute temperature.

The molal (Sb_4O_6) heats of vaporization at the temperatures of the experiment, calculated from the slopes of the lines of Fig. 2 are as follows: for the cubic modification, AH = +47,320 cal.; for the orthorhombic, $\Delta H = +44{,}080$ cal.; and for the liquid antimony trioxide, $\Delta H = +17{,}830$

TABLE III

VAPOR PRESSURE OF ANTIMONY TRIOXIDE

Form of Sb_2O_3	Temp.. °C.	Pressure in mm. of mercury	$\log_{10} p_{\text{mm.}}$
Orthorhombic (metastable)	450	0.010	−2.00
Cubic (stable)	450	.0075	−2.125
Cubic (stable)	475	.0224	−1.650
Cubic (stable)	500	.0625	−1.204
Cubic (stable)	525	.1645	−0.783
Cubic (stable)	550	.406	− .391
Computed Transition Temperature			
Cubic and orthorhombic (stable)	557	0.525	−0.280
Orthorhombic (stable)	575	0.908	− .042
Orthorhombic (stable)	600	2.42	.384
Orthorhombic (stable)	625	3.91	.592
Orthorhombic (stable)	650	7.60	.881
Computed Melting Point			
Orthorhombic (stable)	655	8.50	0.930
Cubic (metastable)	642	(7.43)'	.872
Liquid (stable)	675	10.42	1.018
Liquid (stable)	700	13.32	1.125
Liquid (stable)	725	16.90	1.228
Liquid (stable)	750	20.78	1.318
Liquid (stable)	775	25.93	1.414
Liquid (stable)	800	31.76	1.502
Liquid (stable)	825	(38.36)	1.584
Liquid (stable)	850	(45.9)	1.662
Liquid (stable)	875	(54.8)	1.739
Liquid (stable)	900	(64.6)	1.810
Normal boiling point	1456	(760)	2.881

[a] Values in parentheses are extrapolated from curve.

cal. From these data the molal heat of transition of cubic into orthorhombic oxide is $\Delta H_{830} = +3240$ cal., and the molal heats of fusion are 26,250 cal. for the orthorhombic and 29,490 cal. for the cubic. For convenience of reference, vapor pressures as read from the chart of Fig. 2 are shown tabularly in Table III, which shows the vapor and sublimation pressures of the stable modification at 25'-temperature intervals over the determined range.

Summary

1. The vapor pressures of cubic and orthorhombic solid antimony trioxide have been measured between the temperatures 470 and 650° by the gas saturation method.
2. The vapor pressure of liquid antimony trioxide has been determined over the temperature range from 656 to 800°, using a new type of static balanced tensimeter. These values were checked by direct tensimeter measurement.
3. Heats of vaporization and transformation have been calculated from the vapor pressure data.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

THE IONIZATION CONSTANT OF WATER AT 25° FROM THE ELECTROMOTIVE FORCE OF CELLS WITHOUT LIQUID JUNCTION

BY ELLIOTT J. ROBERTS

RECEIVED JUNE 27, 1930 PUBLISHED OCTOBER 6, 1930

In view of the fact that all previous determinations of the ionization constant of water by the electromotive force method have involved cells containing liquid junctions, it appeared to be worth while to make a determination involving no liquid junctions. This has been accomplished by a new method, the basis of which consists of the measurement of two electrodes of the second kind, directly against each other in a common solution containing ions requisite to the reversibility of both electrodes.

In the present case, the two electrodes of the second kind were Pt,H_2,H_2O,OH^- and $Ag,AgCl,Cl^-$, and the solution in which they were measured was a mixture of sodium hydroxide and sodium chloride. Thus the complete cell was

$$Pt,H_2,NaOH\ (m_1) + NaCl\ (m_2),AgCl,Ag$$

The electromotive force of this cell at 25° may be represented by the equation

$$E = E^\circ_a - E^\circ_b - 0.05915 \log m_{Cl^-}/m_{OH^-} - 0.05915 \log \frac{\gamma_{Cl^-}\alpha_{H_2O}}{\gamma_{OH^-}} \qquad (1)$$

where E_a° is the normal potential of the electrode Pt,H_2,H_2O,OH^- and E_b° is the normal potential of the electrode $Ag,AgCl,Cl^-$. If, now, we define a quantity E' by the equation $E' = E + 0.05915 \log m_{Cl}/m_{OH^-}$, Equation 1 becomes

$$E' = E_a^\circ - E_b^\circ - 0.05915 \log \frac{\gamma_{Cl^-}\alpha_{H_2O}}{\gamma_{OH^-}} \tag{2}$$

and at zero concentration of ions

$$E' = E_a^\circ - E_b^\circ \tag{2*}$$

Furthermore, the extrapolation of the E' values to m = 0 should be linear with the ionic strength in dilute solutions, since the last term in Equation 2 contains a ratio of two activity coefficients. Thus, a series of determinations leading to E' at zero concentration will enable a calculation of E_a° if E_b° is known; but[1]

$$E_a^\circ = -0.05915 \log K_w \tag{3}$$

where K_w is the ionization constant of water in terms of activities. E_b° may be obtained from measurements of cells of the type $Pt,H_2,HCl,AgCl,Ag$ by means of an extrapolation involving the use of the theoretical equation of Hückel.[2] Although measurements of the hydrochloric acid cells have been made at 25° by several investigators,[3] further measurements were deemed advisable to insure a uniformity of technique and to avoid possibility of error due to differences in electrodes. Accordingly, measurements on hydrochloric acid cells as well as sodium hydroxide–chloride cells have been made in the present investigation. These measurements furnish data for calculating E' at zero concentration and E_b°, from which E_a° and K_w follow by Equations 2* and **3.**

Similar measurements with hydrogen and silver chloride electrodes on mixtures of sodium chloride with a weak acid and its sodium salt in equimolal proportions should lead to the ionization constant of that weak acid, provided that the constant has a value lying between 10^{-5} and 10^{-9}; or, if suitable corrections are made for ionization or hydrolysis, the range may be extended to 10^{-4} and 10^{-10}. The principal limitation to the use of this type of cell is that no change of phase shall occur at either of the electrodes due to reaction with the foreign ion.

Experimental Procedure

A Leeds and Northrup Type K potentiometer was used and the working standard cell was repeatedly checked against two cells recently standardized by the Bureau of

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[1] Taylor, "Treatise on Physical Chemistry," D. van Nostrand Co., New York, 1924, p. 800.

[2] (a) Hiickel, *Physik.* Z., 26, 93 (1925); (b) Scatchard, THIS JOURNAL, 47, 2098 (1925); (c) Guntelberg, *Z. physik. Chem.*, 123, 199 (1926).

[3] (a) Noyes and Ellis, THIS JOURNAL, 39, 2532 (1917); (b) Linhart, *ibid.*, 41, 1175 (1919); (c) Scatchard, *ibid.*, 47, 641 (1925); (d) Nonhebel, *Phil. Mag.*, [7] 2, 1085 (1926).

Standards. The two pyrex electrode vessels used were of the U-type, and were adapted to a vacuum technique by having an outlet tube at the base of the silver chloride electrode limb and an inlet tube about one-third of the way up on the hydrogen electrode limb. A three-way cock attached to the inlet tube allowed this to be used for the introduction of both hydrogen and solution. Auxiliary outlets through the rubber stoppers carrying the electrodes assisted in washing and removing gas bubbles. The electrode vessels were permanently mounted in an air thermostat maintained at 25±0.02°, with the inlet and outlet tubes projecting, respectively, through the side and base of the thermostat. Hydrogen prepared by the electrolysis of a 15% solution of sodium hydroxide was passed through pure water at 25° before reaching the electrode vessels. Platinum strips, 0.5 by 2.5 cm. coated with platinum black for two to ten minutes at 150 milliamperes, served as hydrogen electrodes. After each determination they were heated to a white heat before re-use. The silver chloride electrodes were of the Noyes and Ellis type and were used for a number of measurements before being replaced. Recrystallized sodium chloride was added in the required amount to an 0.2 *M* solution of carbonate-free sodium hydroxide, prepared as described by Cornog,[4] and the resultant solution was analyzed for hydroxide and chloride ions. This solution was diluted with carbon dioxide-free distilled water as required. A carefully standardized 0.2 M solution of hydrochloric acid was prepared from distilled acid. The solutions used in the hydrochloric acid measurements were prepared by dilution, both the stock solution and the distilled water being weighed to one part in five thousand. All solutions were freed from dissolved oxygen by boiling in *vacuo* before being drawn into the electrode vessels. correction being made for the water lost. One liter of solution was used for each washing and filling of a cell. The capacity of each cell was 100 cc. The process of washing occupied about thirty minutes, which allowed considerable time for soaking out the silver chloride electrodes. Constant potential was reached one to two hours after starting the hydrogen. Three factors contributed to the elimination of error due to adsorption or reaction of the solutions with glass: namely, the use of pyrex vessels, the rapid attainment of equilibrium, and the approach of the determinations from both more concentrated and more dilute solutions. Removal of dissolved oxygen was shown by Güntelberg[5] to be necessary in the case of hydrochloric acid. In confirmation, results 0.3-0.4 mv. higher were obtained when 0.01 M solutions were introduced into the cells without boiling.

Experimental Results

Table I presents the results of measurements on sodium hydroxide–chloride cells in which the ratio of m_{Cl^-} to m_{OH^-} was within 1% of unity. Column 1 gives the total molality, $m_1 + m_2$; Col. 2, the observed e. m. f. corrected to 1 atm. partial pressure of hydrogen and to unity ratio of m_{Cl^-} to m_{OH^-}, the latter correction amounting to −0.29, −0.10 and −0.08 mv. in the three stock solutions made up.

Table II presents the results of measurements on hydrochloric acid cells. Column 1 gives the concentration of hydrochloric acid in moles per kilo of water in *vacuo,* Col. 2, the observed e. m. f. corrected to 1 atm. partial pressure of hydrogen, and Col. 3, the deviation of the individual E_b° values, as calculated by Equations 5 and 8, from the average of these values (−0.22239).

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[4] Cornog, This Journal, 43, 2573 (1921).

[5] Güntelberg, *Z. physik. Chem.*, 123, 199 (1926).

TABLE I

ELECTROMOTIVE FORCE IN VOLTS AT 25° OF THE CELLS $Pt,H_2,NaOH + NaCl,AgCl,Ag$

Total molality	E' observed	Total molality	E' observed	Total molality	E' observed
0.0126	1.05077	0.0326	1.05081	0.166	1.05101
.0168	1.05081	.0526	1.05081	.203	1.05083
.0170	1.05081	.0844	1.05089	.270	1.05085
.0212	1.05084	.130	1.05082		

TABLE II

ELECTROMOTIVE FORCE IN VOLTS AT 25° OF THE CELLS $Pt,H_2,HCl,AgCl,Ag$

Molality	E observed	$-E^\circ_b$ (Eq. 8) −0.22239 in mv.	Molality	E observed	$-E^\circ_b$ (Eq. 8) −0.22239 in mv.	Molality	E observed	$-E^\circ_b$ (Eq. 8) −0.22239 in mv.
0.001637	0.55424	+0.00	0.010525	0.46156	−0.02	0.03117	0.40871	+0.11
.001932	.54597	+ .04	.010759	.46042	− .08	.03340	.40530	+ .05
.002128	.54116	+ .12	.010965	.45947	− .09	.03358	.40512	+ .13
.002861	.52621	− .02	.011127	.45866	− .18	.03661	.40074	− .08
.003897	.51070	− .09	.011460	.45741	− .01	.04045	.39612	+ .14
.004222	.50695	+ .16	.011708	.45628	− .05	.04130	.39485	− .13
.006073	.48874	+ .01	.014364	.44646	+ .14	.04223	.39396	+ .05
.006117	.48838	+ .01	.015221	.44358	+ .09	.04253	.39363	+ .06
.009159	.46838	− .05	.020542	.42875	− .11	.05076	.38500	− .02
.009395	.46725	+ .08	.020635	.42871	+ .08	.05135	.38444	− .02
.009517	.46659	+ .04	.020684	.42854	+ .02	.06147	.37577	− .02
.009729	.46558	+ .14	.020844	.42826	+ .12	.06230	.37508	− .06
.009736	.46536	− .07	.020891	.42817	+ .14	.08322	.36122	+ .06
.009977	.46408	− .13	.02171	.42608	− .07	.08336	.36097	− .14
.010222	.46287	− .16	.02265	.42425	+ .15	.09018	.35729	+ .01
.010300	.46256	− .09	.02273	.42398	+ .07	.10757	.34887	+ .10
.010400	.46209	− .09	.02653	.41641	+ .00	.13544	.33762	+ .01
.010430	.46191	− .13	.02981	.41062	− .15	.13820	.33679	+ .17

Calculation of Results

The extrapolation of the E' values of Table I to $m = 0$ gives 1.05080 volts. Values of E°_b were calculated by means of the equation

$$-E^\circ_b = E_{\text{obs.}} + 0.1183 \log m + 0.1183 \log \gamma_\pm \qquad (5)$$

The values of $\log \gamma_\pm$ were calculated by means of Hückel's equation, using three different combinations of constants, as follows

$$\text{(a)} \quad \log \gamma_\pm = -\frac{0.5000\sqrt{c}}{1 + 1.4\sqrt{c}} + 0.136\,c - \log(1 + 0.036\,m) \qquad (6)$$

which is the formula used by Güntelberg[5] for his results at 20°

$$\text{(b)} \quad \log \gamma_\pm = -\frac{0.5049\sqrt{c}}{1 + 1.329\sqrt{c}} + 0.1426\,c - \text{bg}\,(1 + 0.036\,\text{m}) \qquad (7)$$

which is the formula used by Scatchard[6] for results at 25°

$$\text{(c)} \quad \log \gamma_\pm = -\frac{0.5044\sqrt{c}}{1 + 1.45\sqrt{c}} + 0.1338\,c - \log(1 + 0.036\,m) - N \qquad (8)$$

where N is the second term of formula No. 107 of Gronwall, La Mer and

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[6] Scatchard, THIS JOURNAL, 47, 2098 (1925).

Sandved,[7] and has a maximum value of 0.09 mv. The two constants 1.45 and 0.1338 were determined by trial, with the aid of Scatchard's[8] results above 0.1 M. The values of c were calculated by means of the equation

$$c_{25^\circ} = M - M\,(0.0029 + 0.0184\,M + 0.0001\,M^2) \qquad (9)$$

which was derived from data in the "International Critical Tables."

The average values for E_b° as calculated by means of the three equations are -0.22247, -0.22235 and -0.22239 volt, respectively, with mean deviations from the average of 0.08, 0.09 and 0.08 millivolt, respectively. The average of the three values, -0.22240 volt, may therefore be used for E_b° (E° of the silver chloride electrodes used). By Equation 2*

$$\mathrm{Pt,H_2,H_2O,OH^-};\ E^\circ = 0.82840 \text{ volt } \pm 0.10 \text{ mv.}$$

Therefore, by Equation 3

$$K_w = (0.988 \pm 0.004) \times 10^{-14}$$

Summary

The ionization constant of water has been determined at 25° from the electromotive force of cells without liquid junction and found to be equal to $(0.988 \pm 0.004) \times 10^{-14}$.

A new method has been outlined for the determination of the ionization constants of weak electrolytes from the electromotive force of cells without liquid junction.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DIVISION OF INORGANIC CHEMISTRY, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE AMMONATES OF COPPER SELENITE[1]

BY LOREN C. HURD, GEORGE I. KEMMERER AND V. W. MELOCHE

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As a part of the study of selenium and its compounds being made at this Laboratory, it was thought that an investigation of the compounds formed by the action of ammonia on the metallic selenates and selenites might yield results of interest. The present report deals with the compounds formed by the action of ammonia on copper selenite.

During the course of an investigation of a number of ammonates of metallic salts, Boutzaureanu[2] prepared a monammonate monohydrate of

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[7] Gronwall, La Mer and Sandved, *Physik. Z.*, 29,358 (1928).

[8] Scatchard, THIS JOURNAL, 47,641 (1925).

[1] Abstracted from a portion of a thesis submitted to the Faculty of the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1929. This work was started under the direction of the late Victor Lenher, continued under the supervision of the late George Kemmerer, and completed under the guidance of Professor V. W Meloche.

[2] Boutzaureanu, Ann. *chim. phys.*, 6, 18, 346 (1889).

copper selenite. His method of preparation was to dissolve copper selenite in ammonium hydroxide and to allow the resulting dark blue solution to evaporate. The residue was a blue product corresponding in composition to the formula $CuSeO_3 \cdot NH_3 \cdot H_2O$.

Preparation of Copper Selenite **Dihydrate.**—The direct neutralization of selenious acid with copper carbonate or precipitated copper oxide yielded a flocculent green precipitate, the color and composition of which varied with the preparation. Boutzaureanu[2] converted this basic salt to the normal dihydrate by subjecting it to the action of a 5% solution of selenious acid in a closed bomb at a temperature of 250° for two hours. It was found that although this method yielded the normal dihydrate, it was usually contaminated with small amounts of elementary selenium. Inasmuch as almost all of the preparations to be described were checked on the weight conversion basis, it was necessary to devise a method of preparation which would yield pure copper selenite dihydrate in large quantities.

The most satisfactory method for the preparation of copper selenite was to add to a hot 15% solution of selenious acid a saturated solution of copper acetate. The flocculent green precipitate first formed immediately redissolved and precipitated the slightly soluble copper selenite dihydrate. The product was filtered on a sintered glass plate, washed with a 1% solution of selenious acid and then with distilled water. Analysis of the air-dried product yielded results in harmony with the calculated values for the dihydrate. In some cases the water content was slightly higher than the calculated percentage. In such cases the selenium and copper content was correspondingly low. The methods of analysis used through the work have been described in an earlier paper.[3]

The Hydrated Ammonates of Copper Selenite

Copper Selenite Diammonate Monohydrate.—Fifty grams of copper selenite dihydrate was dissolved in 50 cc. of concentrated ammonium hydroxide and the solution transferred to an eight-inch pyrex tube. The tube was placed in a thermostat at 60° and a rapid stream of ammonia gas passed into the solution. Following the evaporation of the bulk of the liquid there remained a mass of blue crystals. The product was removed from the tube, transferred to a sintered glass filter and pressed dry by means of a piece of rubber dental dam tied over the top of the funnel. Following the removal of most of the liquid, the product was placed over freshly ignited time for one hour. Analysis of the material yielded results in accord with the calculated values for $CuSeO_3 \cdot 2NH_3 \cdot H_2O$.

Anal. Calcd. for $CuSeO_3 \cdot 2NH_3 \cdot H_2O$: CuO, 32.76; Se, 32.61; NH_3, 14.02. Found: CuO, 32.42; Se, 32.20; NH_3, 14.45 (all av. of 3 detns.).

Copper selenite diammonate monohydrate was a blue crystalline salt, the color of which was slightly lighter than the B shade of the normal tone of Mulliken's color standards.[4] It was very unstable. Traces of moisture caused a liberation of ammonia with

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[3] Hurd and Lenher, THIS JOURNAL, 52, 3857 (1930).

[4] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1904, Color Charts, Vol. I.

the formation of lower ammonates and basic salts. The ammonate was not completely soluble in water but dissolved readily in acids and ammonia solution. It was insoluble in liquid ammonia.

Copper selenite diammonate monohydrate was also prepared by the action of anhydrous ammonia gas on copper selenite dihydrate at 25°. The product was usually slightly moist in spite of prolonged exposure over desiccating agents in an atmosphere of ammonia. The compound when prepared in this manner usually contained slightly more water and ammonia than the calculated amounts.

Passage of ammonia into an ammoniacal solution of copper selenite did not yield a precipitate until the solution was cooled below 10°. Below this temperature a mass of crystals was obtained which when warmed melted to a blue viscous liquid. Analysis of numerous samples did not yield results in harmony with values calculated from any simple formula. Analysis of acid solutions of the product indicated the copper selenite–ammonia ratio to be as 1:3.

Copper Selenite **Monammonate** Monohydrate.—Solutions of copper selenite containing an excess of ammonia were allowed to evaporate slowly at room temperatures. After a short time a green deposit was formed on the sides and bottoms of the crystallizing dishes. Analysis of the product indicated that it consisted essentially of a basic copper carbonate. A few small crystals were deposited over the bulk of the green scale. Analysis of these products yielded results in approximate agreement with values calculated from the formula $CuSeO_3 \cdot NH_3 \cdot H_2O$. However, when solutions of copper selenite in carbon dioxide-free ammonium hydroxide were allowed to evaporate out of contact with air, a large mass of green crystals was obtained. Analysis of this product substantiated the formula assigned by Boutzaureanu.[2]

Anal. Calcd. for $CuSeO_3 \cdot NH_3 \cdot H_2O$: CuO, 35.25; Se. 35.07; NH_3, 7.54 Found: CuO, 35.13; Se, 34.95; NH_3, 7.67 (all av. of 3 detns.).

Copper selenite monammonate monohydrate so prepared was a dark greenish-blue crystalline mass. It was not readily soluble in water but dissolved easily in dilute mineral acids and ammonia solution. It was not altered by prolonged exposure to air and remained unchanged over phosphorus pentoxide. The compound was also prepared by exposing $CuSeO_3 \cdot 2NH_3 \cdot H_2O$ to the air. Ammonia was evolved and analysis of the light green powder remaining indicated that its composition was the same as that of the salt prepared in the manner of Boutzaureanu.[2]

Anal. Calcd. for $CuSeO_3 \cdot NH_3 \cdot H_2O$: CuO, 35.25; Se, 35.07; NH_3, 7.54. Found: CuO, 34.94; Se, 35.05; NH_3, 7.67 (all av. of 3 detns.).

Anhydrous Ammonates of Copper Selenite

Copper Selenite **Diammonate.**—$CuSeO_3 \cdot 2NH_3$ was prepared from $CuSeO_3 \cdot 2NH_3 \cdot H_2O$ in the same manner in which Dennis and Koller[5] prepared $CuSeO_4 \cdot 4NH_3$ from $CuSeO_4 \cdot 4NH_3 \cdot H_2O$. Samples of $CuSeO_3 \cdot 2NH_3 \cdot H_2O$ were placed in a soda lime desiccator and the system held at a pressure of about 15 mm. for six days. Analysis of the residue established the composition of the compound.

Anal. Calcd. for $CuSeO_3 \cdot 2NH_3$: CuO, 35.39; Se, 35.23; NH_3, 15.15. Found: CuO, 35.29; Se, 35.21; NH_3, 15.15 (all av. of 3 detns.).

Copper selenite diammonate is a light blue compound, the color of which matches closely the color GB, tint 1 of Mulliken's charts.[4] The compound is quite stable, samples losing little weight after prolonged desiccation over soda lime or phosphorus pentoxide. When treated with water a basic precipitate was formed and only a small portion of the sample dissolved. It was insoluble in liquid ammonia but reacted with ammonia gas to form higher ammonates.

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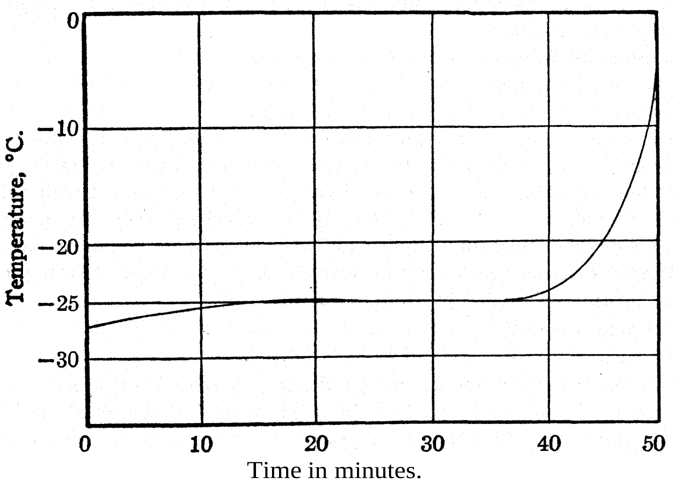
[5] Dennis and Koller, THIS JOURNAL, 41, 949 (1919).

Copper Selenite Triammonate.—It was found that either $CuSeO_3\cdot 2NH_3$ or $CuSeO_3\cdot NH_3\cdot H_2O$ would react with ammonia gas at 0° to form an ammonate of higher ammonia content. In the case of $CuSeO_3\cdot NH_3\cdot H_2O$ water was liberated. From the volume of ammonia absorbed by a given weight of the diammonate it was found that the stable phase at 0° was $CuSeO_3\cdot 3NH_3$.

Twenty grams of $CuSeO_3\cdot NH_3\cdot H_2O$ were treated with a rapid stream of anhydrous ammonia gas at 25° to remove the water and form the anhydrous diammonate. Following the removal of the water the reaction tube was immersed in an ice-bath and treatment with ammonia gas continued. Analysis of the product indicated that the formula of the addition compound was $CuSeO_3\cdot 3NH_3$.

Anal. Calcd. for $CuSeO_3\cdot 3NH_3$: CuO, 32.90; Se, 32.75; NH_3, 21.12. Found: CuO, 32.96; Se, 32.69; NH_3, 20.93 (all av. of 2 detns.).



Pig. 1.—$CuSeO_3\cdot 4NH_3$ to $CuSeO_3\cdot 3NH_3$.

Copper selenite triammonate so prepared had a bright blue color midway between the GB and B normal tone colors of Mulliken's charts.' The ammonate was partially soluble in water. It was relatively unstable and decomposed into the diammonate and ammonia when stored at room temperature. The transition point was found to be in the neighborhood of 19.8'.

Copper Selenite Tetrammonate.—Fifty grams of copper selenite dihydrate was placed in an eight-inch pyrex test-tube and treated with ammonia gas at a temperature of 60°. After eight hours' passage of the gas, the product was removed, crushed and the ammonia treatment continued until the last traces of water had been removed. The tube was then cooled and immersed in a Dewar flask containing liquid ammonia. Passage of gas through the mass was continued until there seemed to be no further absorption. Anhydrous liquid ammonia was then condensed in the tube and the suspension thoroughly stirred. Following removal of the liquid, large samples were quickly removed and sealed into tubes. The tubes were weighed, broken under dilute acid and analysis of the solution made in the usual manner.

Anal. Calcd. for $CuSeO_3\cdot 4NH_3$: CuO, 30.74; Se, 30.59; NH_3, 26.31. Found CuO, 30.39, 30.12; Se, 30.25, 30.01; NH_3, 25.50, 25.86.

Inasmuch as analytical results on preparations of the tetrammonate were seldom in good agreement, it was thought advisable to investigate the warming curve of the system $CuSeO_3.4NH_3$–$CuSeO_3.3NH_3$ between the temperature of boiling liquid ammonia and 0". Accordingly approximately 50 g. of the ammonate was prepared in the manner described. When the excess of ammonia had been removed, the material was quickly mixed with 15 g. of $CuSeO_3 \cdot 3NH_3$ and the system allowed to warm slowly. Temperature was indicated by a toluene thermometer and recordings were taken every thirty seconds. Figure 1 shows a plot of the results obtained in a typical run. The transition point for the system fell at $-25 \pm 1°$. It is interesting to note that the product may be warmed to 0° in the absence of decomposition products. Figure 2 is illustrative of the type of curve obtained when the triammonate inoculation was not made.

Copper Selenite Monammonate.—All anhydrous ammonates of copper selenite were found to decompose at or below 120° to yield $CuSeO_3 \cdot NH_3$. The compound was most conveniently prepared by heating $CuSeO_3 \cdot 2H_2O$ in an atmosphere of ammonia at a temperature of 60". When the water had been removed, the temperature was raised to 120" and the passage of gas continued for several hours. Analysis of the residue established the identity of the salt.

Anal. Calcd. for $CuSeO_3 \cdot NH_3$: CuO, 38.29; Se, 38.11; NH_3, 8.19. Found: CuO, 38.20; Se, 37.99; NH_3, 8.17 (all av. of 3 detns.).

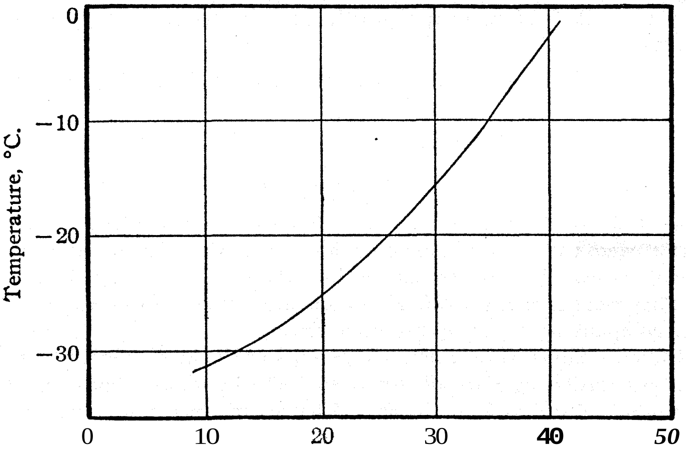


Fig. 2.—Warming curve for $CuSeO_3 \cdot 4NH_3$ in the absence of decomposition products.

$CuSeO_3 \cdot NH_3$ was a green powder when prepared in the manner described. The color was close to the BG, normal tone of Mulliken's charts.' It was insoluble in water and soluble in dilute mineral acids and ammonia solution. $CuSeO_3 \cdot NH_3$ absorbed ammonia below 120° to form higher ammonates. The compound was stable at ordinary temperatures and could be exposed to the air with little alteration. Above 150" $CuSeO_3 \cdot NH_3$ was decomposed with the liberation of ammonia and the production of reduction products of copper selenite.

Summary

1. A new hydrated ammonate of copper selenite, $CuSeO_3 \cdot 2NH_3 \cdot H_2O$, has been prepared and identified.

2. Four new anhydrous ammonates of copper selenite, $CuSeO_3 \cdot NH_3$,

$CuSeO_3 \cdot 2NH_3$, $CuSeO_3 \cdot 3NH_3$ and $CuSeO_3 \cdot 4NH_3$ have been prepared, identified, and their ranges of stability determined.

3. Evidence has been given for the existence of a new hydrated ammonate having the general formula $CuSeO_3 \cdot 3NH_3 \cdot xH_2O$.

4. The work of Boutzaureanu has been checked and the existence of $CuSeO_3 \cdot NH_3 \cdot H_2O$ substantiated.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

THE ACTIVITY COEFFICIENTS OF CESIUM CHLORIDE AND HYDROXIDE IN AQUEOUS SOLUTION[1]

BY HERBERT S. HARNED AND ORION E. SCHUPP, JR.

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The present investigation comprises the evaluation of the activity coefficients at 25° of cesium chloride and hydroxide from measurements of the cells

$$Ag \mid AgCl \mid CsCl(m) \mid Cs_xHg \mid CsCl(0.1) \mid AgCl \mid Ag \qquad \text{(Type I)}$$

and

$$H_2 \mid CsOH(m) \mid Cs_xHg \mid CsOH(0.05) \mid H_2 \qquad \text{(Type II)}$$

Experimental

Cells.—Cells of the type developed by MacInnes and Beattie,[2] Harned,[3] Knoble[4] and Åkerlöf[5] were used. A vacuum technique was always employed and all solutions were boiled in *vacuo* before introduction into the cells. Each cell had a capacity of 100 cc. They were carefully dried before each measurement so as to avoid the waste of solution accompanying the usual method of rinsing.

Electrodes.—Silver–silver chloride electrodes of the kind referred to as Type II in a recent investigation by Harned[6] were used. The hydrogen electrodes were of platinized platinum foil 0.7 by 3 cm. in size. The cesium amalgams were made either by electrolysis of the chloride in a vessel containing a porous cup which served to separate the anode and cathode solutions, or by the electrolysis of cesium hydroxide. Some of the measurements of the cells containing cesium chloride were made with a 0.01% amalgam, while others were obtained by employing a 0.1% amalgam. Both strengths yielded good consistent results, although the potentiometer readings were somewhat difficult to obtain with the 0.01% amalgam. On the other hand, it is important to note that although the 0.1% amalgam gave satisfactory results in the hydroxide solutions, the more dilute amalgam did not.

Cesium Chloride.—This was obtained from the mineral pollucite, $H_2O \cdot 2Cs_2O \cdot 2Al_2$-

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[1] Constructed from part of the thesis presented by O. E. Schupp, Jr., to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy, 1930.

[2] MacInnes and Beattie, THIS JOURNAL, **42,** 1117 (1920).

[3] Harned, *ibid.*, 47, 676 (1925).

[4] Knoble, *ibid.*, **45,** 70 (1923).

[5] Åkerlöf, *ibid.*, 48, 1160 (1926).

[6] Harned, *ibid.*, 51, 417 (1929).

$O_3 \cdot 9SiO_2$, by slightly modifying the methods of Godeffroy[7] and Wells,[8] so as to obtain readily the pure chloride. The finely ground mineral was treated with strong hydrochloric acid and evaporated to small volume on a hot-plate. This strongly acid solution was somewhat diluted, filtered and poured into three to four times its volume of boiling ammonium hydroxide solution in order to precipitate the aluminum. By adding the acid solution to the ammonium hydroxide instead of the reverse process, the precipitate could be very rapidly filtered onto a large Biichner funnel and readily washed with boiling water. The solution was then evaporated to small volume, the ammonium salts removed by nitric acid and the alkali salts converted to the chloride by repeatedly evaporating with hydrochloric acid. This mixture of cesium and other alkali metal chlorides was concentrated and the strongly acid solution treated with antimony trichloride to precipitate the insoluble double salt, $3CsCl \cdot 2SbCl_3$. This salt was hydrolyzed with several changes of water, giving an acid solution containing the cesium chloride together with a little antimony trichloride, but almost free from other alkali salts. Hydrogen sulfide was used to remove the last of the antimony and the solutions evaporated to dryness to obtain the very nearly pure cesium chloride.

For further purification, a concentrated solution of the practically pure chloride was heated with an equivalent weight of iodine and chlorine bubbled into the solution until precipitation of the $CsCl_2I$ ceased. Recrystallization yielded a salt free from other alkali metals, and it was then decomposed into pure cesium chloride by heating. Chloride analyses on the final product calculated to CsCl varied from 99.85 to 100.06% on different samples of salt.

The cesium chloride prepared as described above was used directly, or was converted to the hydroxide. The chloride and hydroxide used in the measurements were recovered in the form of the chloride in the following manner. The solutions were evaporated to dryness on the hot-plate, making certain that an excess of hydrochloric acid was present when hydroxide had been used. This residue was taken up with water and hydrogen sulfide bubbled into the solution to precipitate any dissolved silver, mercury, etc., and the solution filtered and again evaporated. At this point the solution was sometimes evaporated to dryness, the solid scraped out, ground in a mortar, ignited and used for further experiments. At other times the solution was taken nearly to dryness, and the greater part of the salt remaining in solution precipitated as a fine, crystalline product by the addition of considerable 95% alcohol. The material thus obtained was dried in the oven, and then ignited as in the previous case, to obtain the salt ready for use.

Cesium Hydroxide.—Dilute cesium hydroxide—0.1 and 0.05 molal—was prepared by treating a weighed portion of cesium acid sulfate with just enough half normal barium hydroxide solution to react completely, keeping the solutions at all times out of contact with carbon dioxide. The solution thus prepared was filtered through asbestos, carefully tested for sulfate and barium ions, and either sulfuric acid or barium hydroxide added when necessary. This solution was again filtered, analyzed and diluted with boiled distilled water to the desired concentration.

The cesium acid sulfate was obtained by treating the cesium chloride with sulfuric acid, evaporating until all excess sulfuric acid was removed and the acid sulfate slightly decomposed. The salt thus obtained was dissolved in a minimum of hot water and precipitated by the addition of a very considerable quantity of alcohol. This yielded a material which could be dried in the oven, readily ground and mixed and titrated for acid content. From this single analysis, and the assumption that the salt was a mixture of pure cesium acid sulfate and normal cesium sulfate, the amount of barium hydroxide solution required to react with the sulfate in a given amount of salt was calculated, and

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[7] Godeffroy, *Ber.*, 7, 375 (1874).

[8] Wells, *Am. Chem. J.*, 26, 265 (1901).

the two quantities of materials allowed to react. The assumption was evidently correct, for tests of the solutions thus obtained showed only faint traces of either barium or sulfate ions.

The more concentrated cesium hydroxide solution was prepared in a similar way. A hot barium hydroxide solution of about 1.5 molal concentration was prepared and analyzed as accurately as possible. To a weighed amount of this solution an equivalent amount of cesium acid sulfate was added and the two allowed to react. After allowing the barium sulfate to settle, the clear hydroxide solution was siphoned off through an asbestos filter into a second flask, where it was treated with additional barium hydroxide or sulfuric acid until the solution was practically free from an excess of either sulfate or barium ions. This solution was filtered through asbestos as before, analyzed and diluted with boiled distilled water to make solutions of the desired concentrations.

The Activity Coefficient of Cesium Chloride.—Table I contains the electromotive forces, E, of cells of Type I. These are the mean of the number of measurements given in Col. 4. Column 5 shows the maximum variation of the readings from the mean. Column 6 contains the activity coefficients computed by Hiickel's equation[9]

TABLE I

THE ACTIVITY COEFFICIENTS OF CESIUM CHLORIDE SOLUTIONS

1 Molality of CsCl	2 Normality of CsCl	3 E	4 No. cells	5 Max. diff.	6 Hückel	7 Obsd	8 Harned	9 Diff., mv.
0.001	0.001	....		...	0.966	..	..	...
.01	.00997	...		...	.899	..	..	...
.02	.01993	....		...	.864	..	..	...
.05	,04975	−0.03201	2	±0.03	.803	0.802	0.799	0.07
.10	.09931	.00000	.	...	(.747)	(.747)	748	.00
.20	.1978	.03111	5	.16	.685	.685	.688	.00
.50	.4885	.07110	5	.32	.598	.596	.601	.18
.70	.6784	.08568	2	.00	.568	.566	.571	.18
1.0	.9578	.10134	5	.07	(.537)	(.537)	.537	.00
1.5	1.4078	.11925	2	.01	.507	.507	.505	.00
2.0	1.8405	.13228	2	.02	.488	.491	.486	.32
2.5	2.2538	.14214	2	.16	(.476)	(.476)	.475	.11
3.0	2.6511	.15020	1	...	.467	.464	.470	.33

For Hiickel's equation, $A = 0.52$; $B = 0.0160$. For Harned's equation, $\alpha = 0.063$; $\beta = 0.333$; $\alpha' = 0.400$.

$$\log \gamma = -\frac{0.354\sqrt{2c}}{1 + A\sqrt{2c}} + B(2c) - \log(1 + 0.036m) \qquad (1)$$

The constants A and B given in the table were obtained by the usual method from the electromotive forces of the 0.1, 1 and 2.5 molal cells. Column 7 contains the activity coefficient computed from the reference value of 0.747 at 0.1 M obtained from Hiickel's equation by the well-known equation for the cell, namely

$$E = 0.1183 \log \frac{\gamma m}{0.747 \times 0.1} \qquad (2)$$

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[9] Hückel, *Phys. Z.*, 26, 123 (1925).

Further, since we desire the vapor pressures of the solutions for further studies, and since Hückel's equation is complicated for this calculation, we include values computed by Harned's[10] equation

$$\log \gamma = -\beta m^{\alpha'} + \alpha m \tag{3}$$

The constants β, α' and α are given at the bottom of the table. It is clear that in the concentration range of 0.05 to 3 M this equation holds satisfactorily.

The agreement between the observed values and those computed by Hückel's equation is very good as evidenced by the differences in mvs. given in Col. 9. That the activity coefficient of cesium chloride falls in the expected place in respect to the other chlorides is shown by Fig. 1, where the results are plotted along with those obtained by Harned for potassium, sodium and lithium chlorides,[11] and by Randall and Young for hydrochloric acid.[12]

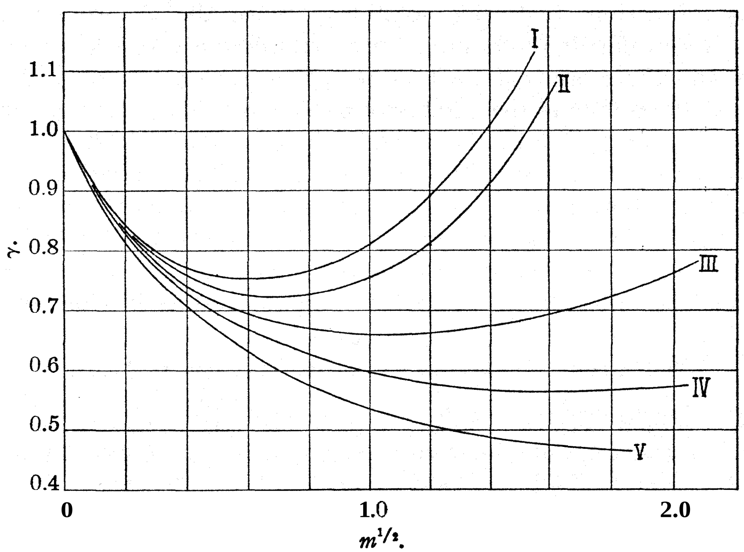

Fig. 1.—The activity coefficients of the alkali chlorides: I, HCl; II, LiCl; III, NaCl; IV, KCl; V, CsCl.

The Activity Coefficient of Cesium Hydroxide in Aqueous Solution.—The electromotive forces of cells of Type II are related to the activity coefficients according to the equation

$$E = 0.1183 \log \frac{\gamma_{\text{CsOH}(m_1)}}{\sqrt{a_{\text{H}_2\text{O}(m_1)}}} \cdot \frac{\sqrt{a_{\text{H}_2\text{O}(m_0)}}}{\gamma_{\text{CsOH}(m_0)}} \times \frac{m_1}{m_0} \tag{4}$$

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[10] Harned, This Journal, 42, 1080 (1920).

[11] Harned, *ibid.*, 51, 416 (1929).

[12] Randall and Young, *ibid.*, 50, 989 (1928).

Since the activity of water is proportional to its vapor pressure, we may write

$$E + 0.05915 \log \frac{p_{H_2O(m_1)}}{p_{H_2O(m_0)}} = 0.1183 \log \frac{\gamma_{CsOH(m_1)}}{\gamma_{CsOH(m_0)}} \tag{5}$$

We are interested in computing both γ_{CsOH}, and γ'_{CsOH}, or γ_{CsOH}/a_{H_2O}. For the former, we must use Equation 5 and for the latter Equation 4, which may be written

$$E = 0.1183 \log \frac{\gamma'_{CsOH(m_1)}}{\gamma'_{CsOH(m_0)}} \times \frac{m_1}{m_0} \tag{4a}$$

Table II contains the observed electromotive forces, E, and the values of γ' computed by Hückel's equation and from the observed electromotive forces by Equation 4a. Column 2 contains measurements of the density of cesium hydroxide solutions. Since the electromotive force values were difficult to obtain, a curve was drawn through the observed values and the more consistent values given in Col. 5 were read off this plot. Column 6 gives the number of measurements of each cell, and Col. 7 the deviation (+) from the mean. The 0.05, 0.5402 and 1.3205 molal cells were used to evaluate the constants in Hückel's equation which are given at the bottom of the table. Column 8 contains the values of γ' computed by Hückel's equation, Col. 9 the values of γ' calculated by Equation 4a by employing 0.831 as the reference value at 0.05 M, and Column 10 similar values computed from the results in Column 5.

TABLE II

THE VALUE OF γ' FOR CESIUM HYDROXIDE IN AQUEOUS SOLUTION

1 Molality of CsOH	2 Density of CsOH	3 Normality of CsOH	4 E meas.	5 E curve	6 No. of cells	7 Max. diff., mv.	8 γ' Hückel	9 γ' Obs.	10 γ' Curve
0.01016	0.99838	0.01013	−0.07638	−0.0775	2	±0.18	0.905	0.925	0.905
,02044	.99969	.02037	.04306	.0433	2	.00	.876	.879	.876
.02550	1.00033	.02541	.03246	.0325	2	.19	.865	.866	.865
.05	1.00343	.04980	.00000	.0000	.	...	(.831)	(.831)	(831)
.09065	1.0087	.09021	+ .02888	+ .0289	2	.02	.800	.804	.804
.1	1.0100	.09951	....	.0336	.	...	.795	...	.799
.232	1.0270	.2303	.07379	.0742	2	.01	.759	.753	.759
.38	1.0458	.3731	....	...		...	.750	...	...
.5402	1.0659	.5326	.11676	.1172	2	.20	(.753)	.747	(.753)
.8902	1.1099	.8715	.14421	.1448	2	.00	.782	.773	.782
1.0	1.1238	.9774	....	.1517	.	...	.795	...	.796
1.3205	1.1626	1.2817	.16865	.16865	2	.04	(.8385)	.8385	(.8385)

Constants for Hückel's equation: A = 0.94; B = 0.0663.

There remains the calculation of γ according to Equation 5, which necessitates a knowledge of vapor pressures of the solutions. The method employed to determine the corrections to the electromotive forces, AE, corresponding to the second member on the left of Equation 5 was the same as that used by Harned.[13] The constants, a, β and d of Equation 3

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[13] Harned, THIS JOURNAL, 47,676 (1925).

were evaluated and the logarithms of the vapor pressure ratios were computed by the equation

$$\ln \frac{p_0}{p} = \frac{m}{55.5}\left[2 + 2.303\alpha m - \frac{4.605\ \alpha'\beta}{\alpha' + 1}\ m^{\alpha'}\right] \qquad (6)$$

From the values of p thus obtained, AE was evaluated. Table III contains the results. Column 2 contains the corrections, AE, Col. 3, the corrected electromotive forces obtained by subtracting AE from the corresponding values of E given in Col. 5, Table II. Column 4 contains the values of γ computed by Hiickel's equation, Col. 5 the values of γ

TABLE III

THE ACTIVITY COEFFICIENT OF CESIUM HYDROXIDE IN AQUEOUS SOLUTION

Molality of CsOH	ΔE	$E_{\text{corr.}}$, curve	γ Huckel	γ_{obs}. measured	γ Harned
0.01016	....	−0.0775	0.905	0.925	..
.02044	....	.0433	.876	.879	..
.0255	....	.0325	.865	.866	..
.05	−0.00000	.00000	(831)	(.831)	(0 831)
.09065	− .00003	.0289	.800	.804	.803
1	.00004	.0336	.795	..	.798
.232	.00016	.0740	.757	.753	.762
.38	,00029	...	.746	..	.749
.5402	.00044	.1168	(747)	.740	(.748)
.8902	.00078	.1440	770	761	.769
1.0	.00090	.1508	.781	..	.780
1 3205	,00125	.1674	(.818)	.818	(819)

Constants for Hiickel's equation: A = 0.97; B = 0.0604.
Constants for Harned's equation: a = 0.152; β = 0.260; a' = 0.362.

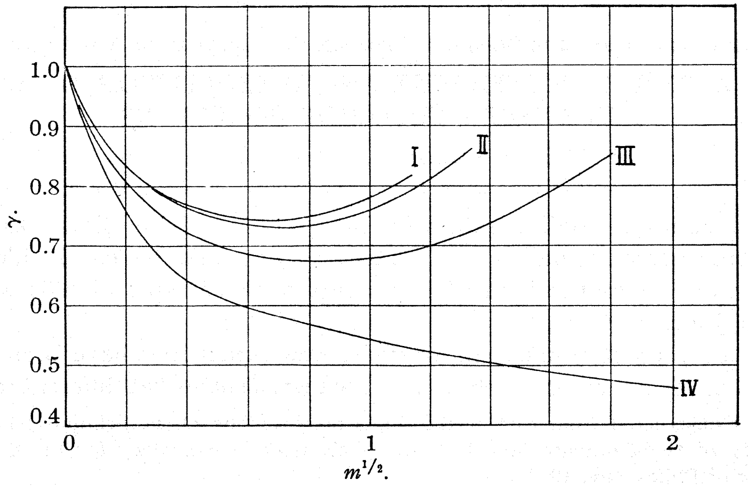

Fig. 2.—The activity coefficients of the alkali hydroxides. I, CsOH; II, KOH; III, NaOH; IV, LiOH.

computed from the observed electromotive forces by employing the reference value of 0.831 at 0.05402 molal concentration. Column 6 contains the values of γ computed by Harned's equation. The constants A, B, α, β and α' are given at the bottom of the table.

In Fig. 2 the activity coefficients of the alkali hydroxides have been plotted against $m^{1/2}$. The activity coefficient of cesium hydroxide lies somewhat higher at all concentrations but close to that of potassium hydroxide. The general rule that the hydroxides show the reverse distribution to the chlorides is verified.

Summary

1. The activity coefficients of cesium chloride and hydroxide in aqueous solution at 25° have been obtained by measurements of the cells,

$$Ag/AgCl/CsCl(m)/Cs_xHg/CsCl(m_0)/AgCl/Ag, \text{ and}$$
$$H_2/CsOH(m)/Cs_xHg/CsOH(m_0)/H_2$$

respectively.

2. The constants of Hückel's equation have been obtained from these results.

3. The constants of Harned's equation have been computed. From these, the vapor pressures of the chloride solutions may be calculated. The vapor pressures of the hydroxide solutions have been computed.

4. Both the chloride and hydroxide activity coefficients are of the expected order of magnitude, and conform with the distribution of the same quantities in the cases of the other alkali chloride and hydroxide solutions

New Haven, Connecticut

[Contribution from the Sterling Chemistry Laboratory of Yale University]

THE ACTIVITY COEFFICIENT AND DISSOCIATION OF WATER IN CESIUM CHLORIDE SOLUTIONS[1]

By Herbert S. Harned and Orion E. Schupp, Jr.

Received June 30, 1930 Published October 6, 1930

In a series of studies, values for the variation of the dissociation and the ionic activity coefficient of water in some uniunivalent halide solutions were computed from measurements of three types of cells without liquid junction.[2]

In the present communication these same quantities have been determined in cesium chloride solutions. Further, a somewhat different method

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[1] Constructed from part of the thesis presented by O. E. Schupp, Jr., to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy, 1930.

[2] (a) Harned, This Journal, 47, 930 (1925); (b) Harned and Swindells, *ibid.*, 48, 126 (1926); (c) Harned and James, *J. Phys. Chem.*, 30, 1060 (1926).

of calculation has been employed which shows that the determined values depend only on strict thermodynamic principles and one experimentally demonstrated proposition. Secondly, as a check, an alternate method has been employed. We shall proceed directly to a consideration of the experimental results, and let the procedure of calculation develop during this discussion.

The Activity Coefficient of Hydrochloric Acid in Cesium Chloride Solutions.—The electromotive forces of the cells

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{HCl}(0.01),\ \mathrm{CsCl}(m) \mid \mathrm{H_2} \mid \mathrm{HCl}(0.01) \mid \mathrm{AgCl} \mid \mathrm{Ag} \qquad \text{(Type I)}$$

are related to the activity coefficients and concentrations involved by the equation

$$E = 0.1183 \log \frac{\gamma_{\mathrm{HCl}}}{0.904} \frac{(m + 0.01)}{0.01} \qquad (1)$$

This double cell was not measured directly but was obtained by subtracting the electromotive force of the cell

$$\mathrm{H_2} \mid \mathrm{HCl}(0.01),\ \mathrm{CsCl}(m) \mid \mathrm{AgCl} \mid \mathrm{Ag} \qquad (E_1)$$

from that, E_0, of the same cell containing 0.01 M hydrochloric acid only. The results are given in Table I. The headings of the columns are self-explanatory. The final column contains the activity coefficients calculated by Equation 1 from the value of 0.904 at 0.01 M given by Randall and Young.[3] The measurements were carried out with the usual type of cell, and the electrodes made in the usual manner. Up to a concentration of 0.7 M cesium chloride the measurements proved to be very satisfactory. At this concentration and above, reproducibility decreases with increasing salt concentration.

TABLE I

THE ACTIVITY COEFFICIENT OF 0.01 MOLAL HYDROCHLORIC ACID IN CESIUM CHLORIDE SOLUTIONS

Molality of CsCl	E. m. f., E_1	Maximum diff., mv.[a]	Number of cells	$E_0 - E_1$	γ, HCl
0.0000	0.46456	±0.09 mv	25	0	0.904
.01	.44846	.07	4	0.00610	.874
.03011	.43296	.07	6	.03160	.835
.07	.41781	.07	3	.04675	.794
.1	.41110	.02	4	.05346	.772
.2	.39739	.04	4	.06717	.729
.4	.38350	.07	4	.08106	.684
.7	.37162	.05	2	.09294	.655
1.0	.36353	.31	5	.10103	.643
1.3434	.35643	.02	2	.10813	.6375
1.5	.35363	.03	2	.11093	.638
2.0	.34610	.08	2	.11846	.640
3.0	.33325	.07	2	.13131	.671

[a] Represents the maximum difference of any measurement from the mean value recorded in Column 2.

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[3] Randall and Young, THIS JOURNAL, 50, 989 (1928).

That the results obtained are in accord with expectations is shown by Fig. 1, in which γ of hydrochloric acid in alkali halide solutions is plotted against the square root of the ionic strength. The cesium chloride curve falls in the expected position.

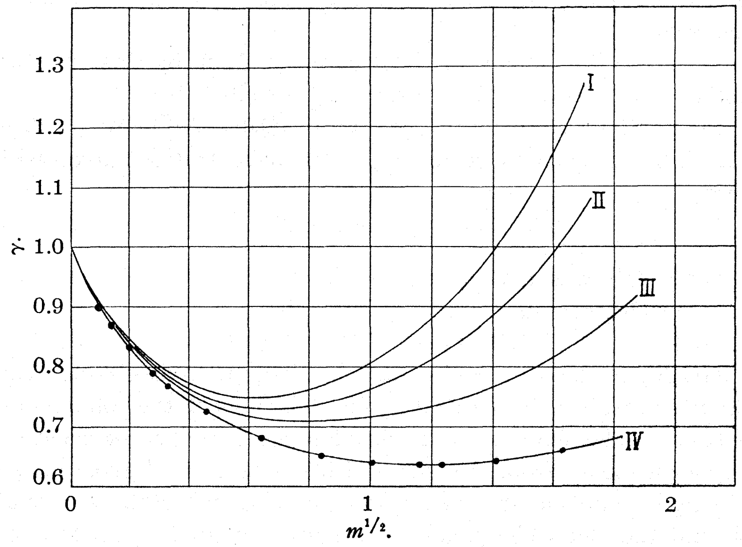

Fig. 1.—The activity coefficient of hydrochloric acid in alkali chloride solutions: I, LiCl; II, NaCl; III, KCl; IV, CsCl.

The Activity Coefficient of Cesium Hydroxide in Cesium Chloride Solutions.—The electromotive forces of the cells

$$H_2 \mid CsOH(m_0),\ CsCl(m) \mid Cs_xHg \mid CsOH(m_0) \mid H_2$$

may be employed to determine the activity coefficient of cesium hydroxide in cesium chloride solutions by means of the equation

$$E = 0.1183 \log \frac{\gamma'}{\gamma'_0} \frac{(m_0 + m)}{m_0} \qquad (2)$$

$$= 0.1183 \log \frac{\gamma}{\gamma_0} \frac{(m_0 + m)}{m_0} + 0.06915 \log \frac{a_{H_2O(0)}}{a_{H_2O}} \qquad (3)$$

γ is equal to $\sqrt{\gamma_{Cs}\gamma_{OH}}$, γ' equals $\sqrt{\gamma_{Cs}\gamma_{OH}/a_{H_2O}}$ in the salt solutions, and γ'_0 and γ_0 are like quantities in the pure hydroxide solution of concentration m_0. To evaluate the second member on the right of Equation 3, we have made use of the method of Harned[4] for evaluating the vapor pressure ratio of cesium chloride solutions. The constants of Harned's equation were obtained from Table I, and the calculations made by Equation 6 of a previous communication.[5] This necessitated the assumption that the vapor pressures of 0.05 and 0.1 M cesium hydroxide solutions

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[4] Harned, This journal, 44, 252 (1922).

[5] Harned and Schupp, *ibid.*, 52, 3886 (1930).

were the same as those of the corresponding strengths of the chloride solutions. Since the term under consideration is small, this assumption introduces no appreciable error. Two series of results were obtained with cesium hydroxide solutions of **0.05** and **0.1** M, respectively, of which the **0.05** series occurs in Table II. Since it was necessary for further calculation to know γ' at concentrations corresponding to the hydrochloric acid–cesium chloride system, the observed electromotive forces were used to construct a curve from which the results in Col. **3** were obtained. Column 5 contains the vapor pressure ratio from which the second member in the right of Equation **3** was computed.

TABLE II

THE VALUES OF $\gamma'_{CsOH} = \gamma_{CsOH}/a_{H_2O}$ AND THE TRUE ACTIVITY COEFFICIENT OF 0.05 MOLAL CESIUM HYDROXIDE IN CESIUM CHLORIDE SOLUTION ($m_0 = 0.05$)

m, CsCl	E, measured	E, curve	γ' curve	$p_s/p_{0.05}$	γ curve
0.0000	....	....	0.831	1.000	0.831
.09563	0.02241	0.02240	.753	0.997	.752
.1	....	.02300	.751	.997	.750
.1028	.02344	.02340	.750	.997	.749
.1522	.02933	.02925	.730	.995	.728
.2	....	.03370	.716	.994	.714
.3511	.04353	.04350	.684	.989	.681
.3534	.04358	.04355	.683	.989	.679
.5	....	.05020	.666	.985	.661
.5479	.05197	.05200	.661	.983	.656
.7058	.05690	.05718	.650	.978	.643
.7269	.05863	.05780	.649	.978	.642
.9411	.06337	.06350	.642	.972	.633
1.00	....	.06493	.642	.970	.632
1.1752	.06983	.06883	.641	.965	.630
1.2835		.07108	.642	.961	.629
1.5	....	.07516	.645	.955	.630
1.7077	.07797	.07860	.647	.949	.631
2.1253	.08660	.08460	.654	.937	.633
3.6896	.10248	.10248	.706	.887	.665

The Ionic Activity Coefficient and Dissociation of Water in Cesium Chloride Solutions.—It has been shown by Harned[6] that even at high concentrations log γ of hydrochloric acid in a uni-univalent chloride solution at constant total molality varies linearly with the acid concentration. This statement is given by the equation

$$\log \gamma = \alpha m_1 + \log \gamma^0 \tag{4}$$

in which α is a constant, m_1 is the acid concentration and log γ^0 is the logarithm of the activity coefficient of hydrochloric acid at zero concentration in the halide solution of concentration m. Harned and Harris[7]

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[6] **Harned, THIS JOURNAL, 48,326 (1926).**

[7] **Harned and Harris, *ibid.*, 50,2633 (1928).**

found that in the case of very concentrated sodium and potassium hydroxide solutions there is a small deviation from this law. This makes no theoretical difference since the only information we require is the value of log γ^0, and, consequently, if the results can be extrapolated to zero concentration of hydroxide by a function which fits the experimental material, the data necessary for our calculation are available. In the present instance we make no error greater than the experimental by assuming that Equation 4 represents the correct relationship both in the case of the acid and hydroxide.

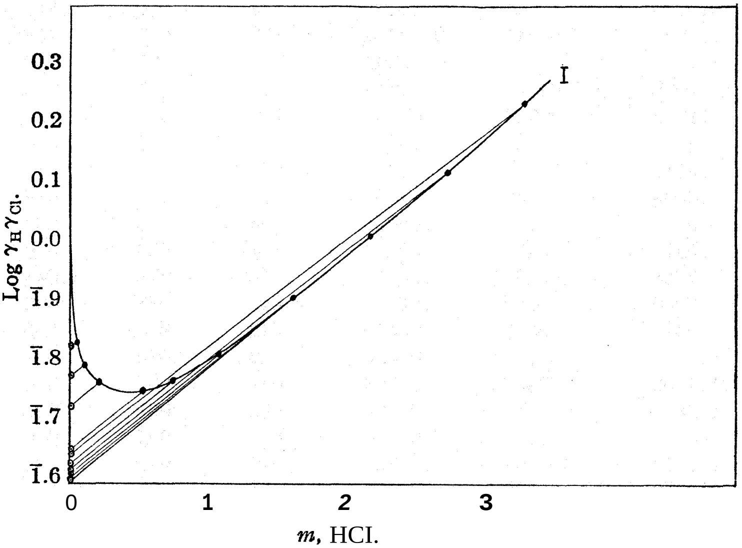

Fig. 2.—m_{HCl}– log $\gamma_H\gamma_{Cl}$ plots at constant total molalities.

In Fig. 2 the logarithm of the square of the activity coefficient of hydrochloric acid in pure aqueous solution (shaded circles) and of 0.01 M hydrochloric acid in cesium chloride solutions of the same total concentration (circles) are plotted against the acid concentration. The straight lines are drawn through the corresponding points at the same constant total molality. The parallel character of these plots leaves nothing to be desired. A short extrapolation to zero acid concentration gives 2 log γ^0 or log $\gamma^0_{H^+}\gamma^0_{Cl^-}$.

In Fig. 3 similar plots have been drawn in the case of cesium hydroxide and the hydroxide–chloride results. The extrapolation gives us the value of 2 log $\gamma^{0\prime}$ or log $\gamma^0_{Cs^+}\gamma^0_{OH^-}/a_{H_2O}$.

It is very important to observe that both $\gamma^0_{H^+}\gamma^0_{Cl^-}$ and $\gamma^0_{Cs^+}\gamma^0_{OH^-}/a_{H_2O}$ are now known in the pure aqueous cesium chloride solutions. Consequently, they may be multiplied to obtain $\gamma^0_{H^+}\gamma^0_{OH^-}\gamma^0_{Cs^+}\gamma^0_{Cl^-}/a_{H_2O}$. If this quantity be divided by $\gamma^0_{Cs^+}\gamma^0_{Cl^-}$ which. we have already evaluated in a previous communication,[5] we obtain $\gamma^0_{H^+}\gamma^0_{OH^-}/a_{H_2O}$, the ionic activity coefficient product of water in cesium chloride solutions, which we shall denote by $K_{\gamma(s)}$. This method is free of all assumptions extraneous to exact thermodynamics other than the use of Equation 4 to extrapolate to zero concentration of acid or hydroxide. The necessary condition for this calculation is that at constant molality the log γ may be extrapolated to zero acid or hydroxide concentration.

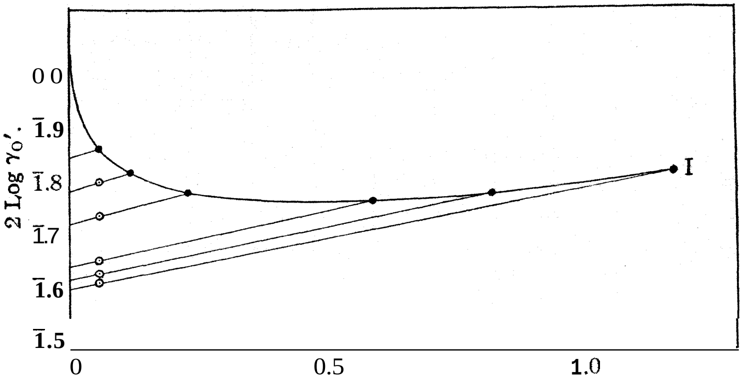

Fig. 3.—m_{CsOH}– **log** $\gamma_{Cs}\gamma_{OH}/a_{H_2O}$ **plots at constant total molalities.**

The thermodynamic equilibrium for the dissociation of water into ions is given by the equation

$$K = K_{\gamma(s)}\, m_{H^+} m_{OH^-} \tag{5}$$

Therefore, since $K_{\gamma(s)}$ has been computed, the variation of the dissociation of water with change in salt concentration may be evaluated. The results are given in Table III. Column 1 contains the total concentration of acid and salt, or hydroxide and salt; Col. 2 the value of γ^0_{HCl},

TABLE III

THE ACTIVITY COEFFICIENT AND DISSOCIATION OF WATER IN CESIUM CHLORIDE SOLUTIONS

1	2	3	4	5	6	7	8
m, CsCl	γ^0_{HCl}	$\gamma^{0'}_{CsOH}$	γ_{CsCl}	$K_{\gamma(s)} = \frac{\gamma_{H^+}\gamma_{OH^-}}{a_{H_2O}}$	$\frac{1}{a_{H_2O}} = \frac{p_0}{p_s}$	$\sqrt{\gamma_{H^+}\gamma_{OH^-}}$	$m_{H^+} = m_{OH^-}$
0.05	0.822	0	0.803	0	1.0017		
.1	.777	0.765	.747	0.634	1.0033	0.795	1.259×10^{-7}
.2	.731	.720+	.685	.591	1.0065	.766	1.305
.5	.671	.663	.598	.552+	1.0158	.738	1.350
.7	.655	.646	.568	.555	1.0220	.744	1.346
1.0	.642	.636	.537	.577+	1.0312	.748	1.320
1.5	.636	..	.507	..	1.0471	..	...
2.0	.638	..	.488	..	1.0636	..	...
2.5	.648	..	.476	..	1.0810	..	...
3.0	.669	..	.467	..	1.0995	..	...

Col. 3 that of $\gamma^{0\prime}_{CsOH}$, Col. 4 γ_{CsCl} and Col. 5 the computed value of . Column 6 contains the values of the activity of water calculated from the vapor pressures by the method of Harned. Column 7 contains the values of $\sqrt{\gamma_{H^+}\gamma_{OH^-}}$, and Col. 8 the values of the hydrogen- or hydroxyl-ion concentrations computed by Equation 5, and the value of 1.005×10^{-14} for the dissociation constant of water.

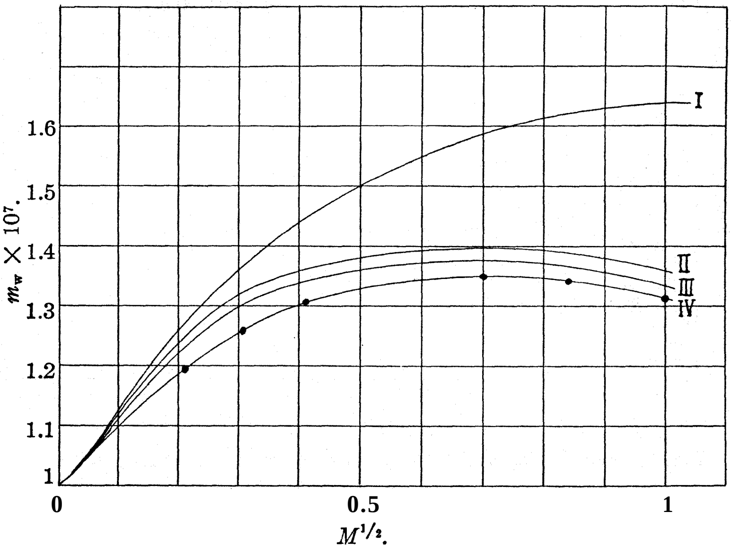

Fig. 4.—The hydrogen- or hydroxyl-ion concentrations in aqueous alkali chloride solutions: I, LiCl; II, NaCl; III, KCl; IV, CsCl.

In Fig, 4 are plotted the values of m_w for the cases of the alkaline chlorides up to 1.0 molal. The results for cesium chloride solutions conform to the expected distribution and show the characteristic maximum.

An Alternate Method of Evaluating the Ionic Activity Coefficient Product in a Salt Solution.—The electromotive force of the cell

$$H_2 \mid CsOH(m_0), CsCl(m) \mid AgCl \mid Ag$$

is given by the equation[8]

$$E = E_0 - 0.05915 \log \gamma_{H^+}\gamma_{Cl^-}m_{H^+}m_{Cl^-} \qquad (6)$$

If we substitute for m_{H^+}, its values derived from the thermodynamic equation for the dissociation of water into ions, namely, $Ka_{H_2O}/\gamma_{H^+}\gamma_{OH^-}m_{OH^-}$, we obtain

$$\left[E + 0.05915 \log \frac{m}{m_0} - E_0\right] = -0.05915 \log Ka_{H_2O} - 0.05915 \log \frac{\gamma_{H^+}\gamma_{Cl^-}}{\mathrm{YE}+\sim \mathrm{OH}-} \qquad (7)$$

E_0 is the standard electromotive force of the cell, which we **take** to be 0.2225, and K is the dissociation constant of water. If we plot the left-

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[8] The first measurements of this type of cell were made in this Laboratory by Dr. Elliott J. Roberts, This Journal, 52, 3877 (1930).

hand member of this equation against μ, its value at zero μ is equal to 0.05915 log K, since at zero ionic strength a_{H_2O} is unity and by reason of the definition of activity coefficients the second member on the right of the equation vanishes. If we rearrange this equation as follows

$$0.05915 \log \frac{\quad}{a_{H_2O}} = E - E_0 + 0.05915 \left[\log \frac{m}{m_0} + \log K + \log \gamma_{H^+}\gamma_{Cl^-}\right] \qquad (8)$$

it is clear that the ionic activity coefficient product of water, $\gamma_{H^+}\gamma_{OH^-}/a_{H_2O}$, in the cesium chloride solution may be evaluated, since $\gamma_{H^+}\gamma_{Cl^-}$ in this salt solution may be obtained from Table III.

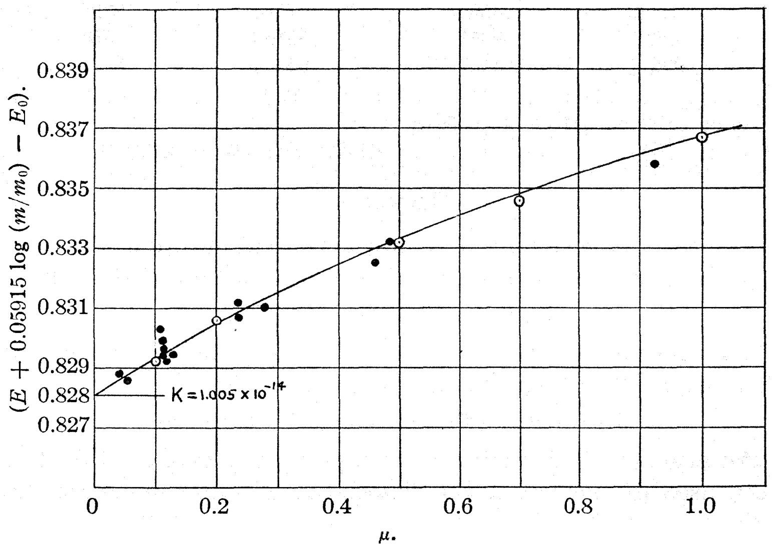

Fig. 5.—Plot of the left side of Equation 7 against the ionic strength.

The cell measurements are given in Table IV, Col. 3. Column 4 contains the values of $(E + 0.05915 \log (m_{Cl^-}/m_{OH^-}) - E_0)$ obtained from them. Even though careful vacuum technique was employed, the measurements were not entirely satisfactory. The electromotive force rose quickly to a maximum and then slowly fell off. The maximum values were recorded. We have, therefore, not employed the results to compute $\gamma_{H^+}\gamma_{OH^-}/a_{H_2O}$. On the other hand, we have computed the value of $(E + 0.05915 \log (m_{Cl^-}/m_{OH^-}) - E_0)$ from the values of $\gamma_{H^+}\gamma_{Cl^-}$ contained in Table I, $\gamma_{H^+}\gamma_{OH^-}/a_{H_2O}$ given in Table III and the value of 10^{-14} for K. In Fig. 5 we have plotted these values which are given in Table IV against the ionic strength, μ (circles). The inked in circles are the results obtained by the second method and given in Col. 4, Table IV. Up to 1.0 *M* the agreement with our previously determined values is good although there is a scattering of ±0.5 mv. in the results.

TABLE IV

CALCULATIONS ACCORDING TO EQUATION 7

m, CsOH	m, CsCl	E. m. f.	$(E + 0.05915 \log (m/m_0) - E_0)$
0.02214	0.02113	1.05255	0.8288
.02204	.03184	1.04162	.8286
.02228	.07492	1.02101	.8297
.02237	.08724	1.01756	.8301
.02202	.09391	1.01470	.8295
.02238	.2330	0.99331	.8310
.02203	.2558	.99047	.8310
.02216	.4377	.97835	.8325
.02232	.4596	.97724	.8325
.02225	.9351	.96193	.8354
.02211	1.3467	.95404	.8371

μ	0.1	0.2	0.5	0.7	1.0
From results of Table III $(E + 0.05915 \log (m/m_0) - E_0)$	0.8292	0.8306	0.8332	0.8346	0.8367

Summary

1. The activity coefficient of hydrochloric acid in cesium chloride solutions at 25° has been determined from measurements of the cells

$$H_2/HCl(m_0),\ CsCl(m)/AgCl/Ag$$

2. The activity coefficient of cesium hydroxide in cesium chloride solutions at 25° has been obtained from the cells

$$H_2/CsOH(m_0),\ CsCl(m)/Cs_xHg/CsOH(m_0)/H_2$$

3. An exact method, similar to that previously employed by Harned, has been used for computing the dissociation of water in cesium chloride solutions.

4. Another method for determining the ionic activity coefficient product and dissociation of water in salt solutions has been described which employs cells of the type

$$H_2/MOH(m_0),\ MCl(m)/AgCl/Ag$$

Measurements of such cells containing cesium hydroxide and chloride have been made, and it is shown that the results conform with those of the method previously used.

5. The values for the dissociation of water in cesium chloride solutions conform with those previously obtained in the cases of the other alkali halides.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

THE ACIDITY OF MONO AND DIAMMONIUM PHOSPHATES

BY T. R. BALL

RECEIVED JUNE 30, 1930 PUBLISHED OCTOBER 6, 1930

It is well known that many samples of diammonium phosphate contain varying amounts of the mono salt. The only test bearing upon the ammonia–phosphate ratio in the diammonium salt which the writer has been able to find is that of the Committee on Analytical Reagents of the American Chemical Society.[1] According to this test, 1 g. of the salt in 10 ml. of water should give a pink color with 2 drops of phenolphthalein solution. This is in no sense a measurement of P_H. The salt effect on the indicator is unknown and the intensity of the color is not specified. The present paper presents data upon the P_H of mono and diammonium phosphates. For both salts in dilute solutions this was obtained by titration of phosphoric acid with ammonia, and in addition the P_H of pure diammonium phosphate at various concentrations was measured with the hydrogen electrode. For higher concentrations, the colorimetric indicator method has been used.

Materials and Procedures

An approximately 0.10 *N* solution of phosphoric acid was made by dilution of a high grade analyzed sample, and its weight normality as a dibasic acid was determined by conversion to magnesium pyrophosphate.

49 915 g. of soln. yielded 0.2854 g. of $Mg_2P_2O_7$; wt n. = 0.1027
49 943 g. of soln. yielded 0.2854 g. of $Mg_2P_2O_7$; wt. n. = 0.1026

A solution of freshly distilled ammonia was used in the titration of the phosphoric acid. It was standardized roughly against hydrochloric acid. In titrating phosphoric acid with ammonia, using a hydrogen–calomel electrode system, the first break in the curve, corresponding to the monoammonium salt, is so sharp as to make the accurate standardization of the ammonia unnecessary. Having determined the volume of reagent required to produce $NH_4H_2PO_4$, it is only necessary to double this to get the point on the curve corresponding to $(NH_4)_2HPO_4$. Because of the volatility of ammonia, this procedure seemed advisable. All e. m. f. measurements were made with a Leeds and Northrup students' potentiometer.

It is impossible to titrate in an open vessel in a stream of hydrogen because of the loss of ammonia in the more alkaline solutions. Consequently a rocking electrode vessel was designed consisting of a pyrex tube 13.5 cm. long and 4.3 cm. in diameter, having a capacity of 160 ml. This tube was sealed at both ends and had three tubulatures in the side for the insertion of a hydrogen electrode, a buret and a salt bridge. It was mounted horizontally on a small shelf attached to a vertical strip of wood 120 cm. long, which served as a pendulum, with its center of oscillation just below the shelf. A strip of sheet brass, with sharpened edges, ran through the wood to serve as a knife-edge which had bearing upon a metal arm clamped to the edge of the laboratory table. A heavy lead weight was attached to the lower end of the pendulum to lower the center of gravity. The huret was supported by clamps to that portion of the strip which projected above the electrode vessel. A hydrogen electrode of platinized platinum was inserted through a

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[1] *Ind. Eng. Chem.*, 19, 645 (1927).

rubber stopper in tubulature No. 1 and a fine-tipped buret in No. 2. A potassium chloride bridge making contact with the calomel electrode, passed through one hole of a rubber stopper in No. 3. This bridge had a glass stopcock which was kept closed except while the e. m. f. measurement was being taken. A 30.5-cm. length of soft rubber tubing in the bridge and also in the hydrogen line gave sufficient flexibility to cause no interference with the rocking of the electrode. A hydrogen exit tube in the second hole of stopper No. 3 dipped about 1 mm. beneath the surface of mercury in a small vial standing upright on the shelf to prevent back-diffusion of air when the hydrogen stream was cut off. In operating, a weighed quantity of the phosphoric acid solution was placed in the vessel and a rapid stream of purified tank hydrogen was passed for about thirty minutes. By swinging the pendulum the vessel was rocked through an angle sufficiently large to cause complete submersion of the hydrogen electrode. Readings were taken at intervals until equilibrium was established and at this point the hydrogen stream was cut off and the titration started by running in ammonium hydroxide from the buret.

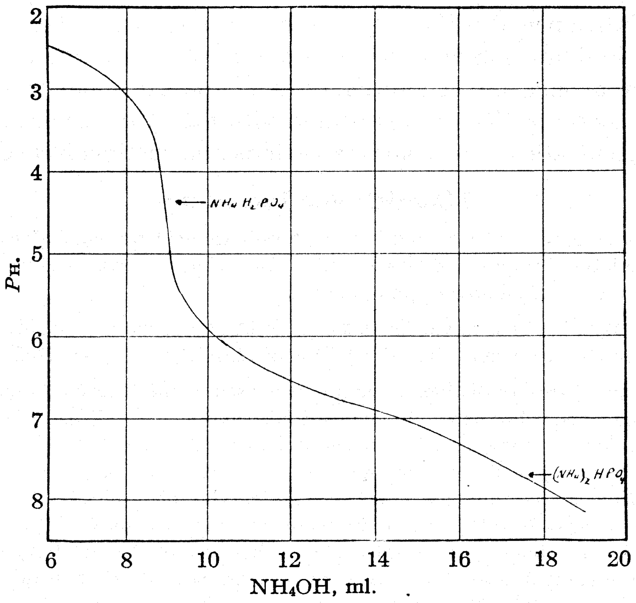

Fig. 1.—Titration curve of phosphoric acid with ammonia.

One source of error that was anticipated with this set-up was the diffusion of ammonia from the buret tip. A very slight upward drift in the potential was observed if the hydrogen electrode was left for some time without intermittent, complete submersion, but by rocking the vessel several times, the original reading could be obtained.

Two curves were run, one of which is shown in Fig. 1. The P_{H} of monoammonium phosphate was found to be 4.35 in each case. It will be noted that there is no break at the equivalence point for diammonium phosphate, because of the hydrolysis of the salt.[2] By finding the point on the curve corresponding to twice the volume of ammonia required to produce the mono salt, the P_{H} of the diammonium salt could be determined. Each curve showed a P_{H} of 7.75 for this salt. The concentrations of the diammonium phosphate were 1.65 and 4.34 g. per liter, respectively, at the end-points

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[2] Buchanan and Winner, *J Ind.* Eng. *Chem.*, 12,448 (1920).

of the two titrations. These values will be referred to later in connection with the effect of concentration upon the acidity.

The test of the Committee on Analytical Reagents makes use of a solution containing 1 g. of diammonium phosphate in 10 ml. The above titration method could scarcely be applied to such high concentrations. Consequently, a high grade. analyzed, commercial sample of diammonium phosphate was carefully analyzed for ammonia and phosphorus in order to establish the ratio of these two constituents. Difficulty was encountered in getting check results, especially for ammonia, when small samples of the dry salt were taken. This was undoubtedly due to the fact that the salt was not uniform. Finally, a 25-g. sample was diluted to 250 ml. and the solution weighed. Weighed portions of this solution were analyzed for phosphorus by conversion to magnesium pyrophosphate, and for ammonia by distillation into standard acid. Five analyses which did not differ from the mean by more than 0.15% showed 0.007553 mole of phosphorus per gram of salt; calcd. for $(NH_4)_2HPO_4$, 0.007568 mole per gram. Two determinations of ammonia showed 0.01481 and 0.01481 mole per gram; calcd., 0.01514 mole per gram; ratio $NH_4 : P = 1.96:1$. The salt, in addition to being deficient in ammonia, probably contained enough water to lower the percentage of phosphorus.

A solution was made from the original salt by taking a sample of sufficient size to yield exactly 50 g. of pure diammonium phosphate after fortification with the calculated amount of standard ammonia required to make up the deficiency. This solution was then diluted to 500 ml. to give a solution of the concentration used by the Committee. Four other solutions were made from this by successive dilution and the PH of each was determined by the hydrogen electrode in the rocking vessel already described. For these determinations, the apparatus was modified by inserting a two-holed stopper in tubulature No. 2. One hole carried the buret and the other a siphon tube with a pinchcock. This made it possible to remove the solutions through the siphon and replace them by others from the buret without admitting air. The vessel was flushed out with at least three 50-ml. portions of solution before the PH measurements were made. The PH of the most concentrated solution was also determined colorimetrically with cresol red and phenol red. The results are shown in Table I.

TABLE I

THE PH OF DIAMMONIUM PHOSPHATE AT VARIOUS CONCENTRATIONS

Soln.	Concn., g. per liter	Concn., moles per liter	PH Hydrogen elect.	Cresol red	Phenol red
1	100	0.7568	8.01	8.3	8.1
2	40	.3027	7.89		
3	20	.1514	7.84		
3a	4.34	.0328	7.75[a]		
4	4.00	.0303	7.77		
4a	1.65	.01249	7.75[a]		
5	0.80	.00605	7.72		

[a] Solutions 3a and 4a were produced by titration.

The data of Table I are plotted in Fig. 2. The dots on the curve are points found by dilution of the pure salt and the crosses designate titration data. The maximum deviation from the smooth curve is 0.025 unit of PH. From 0.8 to 20 g. per liter the PH is almost a linear function of log $1/C$; above this concentration the PH increases rapidly to 8.01 at 100 g. per liter.

The salt error for cresol red is very marked in the concentrated solution

(100 g. per liter), being +0.29 unit of *P*H. Ramage and Miller[3] have noted an effect of +0.25 unit on this indicator in solutions of alkali chlorides of 2.5% concentration, and Wells'[4] data show errors of the same order. Phenol red shows a salt error of only 0.09 unit. Either of these indicators could be used empirically to test the ammonia–phosphate ratio, but neither gives the correct PH in solutions of the concentration used by the committee.

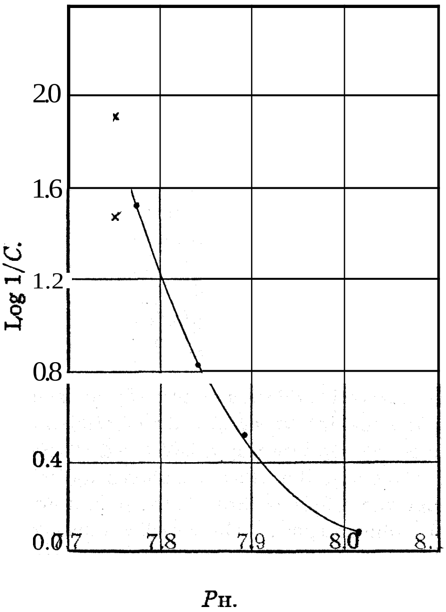

Fig. 2.—The effect of concentration upon the *P*H of $(NH_4)_2HPO_4$ solutions.

Ten ml. of the pure diammonium phosphate solution (1 g. in 10 ml.) gave a pink color with 2 drops of phenolphthalein, (10 g. in 1 liter of 95% alcohol) which was removed by 0.30 ml. of 0.10 *N* sulfuric acid. The solution contained a total of 0.007568 mole of the diammonium salt. Only 0.00003 mole, or 0.38%, would be converted into the mono salt by the acid required to decolorize the solution. The test of the Committee, therefore, appears to be sufficiently accurate for all practical uses. A word might be added regarding the use of diammonium phosphate as a precipitant for zinc. Ball and Agruss[5] have shown that zinc is best precipitated at a *P*H between 6.5 and 6.9. The titration curve of Fig. 1 shows that in this range of acidity from 30 to 50% of the excess phosphate would exist as the monoammonium salt. Obviously the usual precaution of applying the phenolphthalein test is not necessary.

Summary

The *P*H values of diammonium phosphate solutions, ranging in concentration from 0.8 to 100 g. per liter, have been determined.

At concentrations up to 20 g. per liter, the *P*H is almost a linear function of log 1/*C* and increases with the concentration. Above 20 g. per liter the *P*H increases rapidly.

The test of the Committee on Analytical Reagents of the American Chemical Society is accurate, within about 0.4%.

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[3] Ramage and Miller, THIS JOURNAL, 47, 1230 (1925).

[4] Wells, *ibid.*, 42, 2160 (1920).

[5] Ball and Agruss, *ibid.*, 52, 120 (1930).

Cresol red shows a salt error of +0.29 unit when applied to the solution used by the Committee. Phenol red shows an error of 0.09 P_H unit,

In dilute solution, monoammonium phosphate has a P_H of 4.35.

A simple, inexpensive type of rocking electrode has been described.

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION OF THE U. S. BUREAU OF MINES]

EXPLOSIONS IN DETONATING GAS MIXTURES. I. CALCULATION OF RATES OF EXPLOSIONS IN MIXTURES OF HYDROGEN AND OXYGEN AND THE INFLUENCE OF RARE GASES[1]

BY BERNARD LEWIS[2] AND JAMES B. FRIAUF[3]

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Historical

In the year 1381, Berthelot and Vieille[4] and independently Mallard and Le Chatelier[5] announced the discovery of the propagation of explosions in gas mixtures with speeds enormously greater than had been measured previously. These investigators were able to measure the speeds in a number of different mixtures by means of chronoelectric[6] and photographic[7] methods, respectively. Since then, Dixon and others[8] have continued these studies and have measured the velocity of propagation of the detonation wave in a large number of gas mixtures.

Properties of the Detonation Wave.—When certain inflammable gas mixtures are ignited at one end of a uniform tube, the initial slow movement of the flame is rapidly accelerated to a high speed, which remains constant, regardless of the length of the tube. The term "detonation wave" is applied to the propagation of a disturbance at this constant

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) Read before American Chemical Society at Atlanta, Georgia, April, 1930.

[2] Physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

[3] Consulting physicist, U. S. Bureau of Mines. Pittsburgh Experiment Station, Pittsburgh, Pa.

[4] Berthelot and Vieille, *Compt. rend.*, 93, 18 (1881).

[5] Mallard and Le Chatelier, *ibid.*, 93,145 (1881).

[6] Berthelot and Vieille, *ibid.*, 94, 101, 149,822 (1882); 95, 151, 199 (1882); *Ann. chim. phys.*, 28,289 (1883).

[7] Mallard and Le Chatelier, Ann. *des Mines*, [8] 4, 274, 335 (1883); *Compt. rend.*, 130,1755 (1900); 131, 30 (1900).

[8] H. B. Dixon, *Phil. Trans. Roy. Soc.*, 184A, 97 (1893); 200A, 315 (1903). See Bone and Townend, "Flame and Combustion in *Gases*," 1927, pp. 511–518, for more complete list of references.

speed. The following are among its more important properties. (1) When established, the detonation wave propagates with a constant velocity which depends upon the chemical and. percentage composition of the gas mixture. (2) The speed is independent of the material of which the tube is made. **(3)** The speed is independent of the diameter of the tube, if this is larger than a small limiting value. (4) The speed is practically independent of the initial pressure and temperature of the gas mixture. A three-fold variation in pressure near atmospheric or a variation in temperature from 10 to 100° introduces only a slight alteration in speed. (5) The speed is independent of conditions in the rear of the wave. It is immaterial whether inflammation is started at the closed or open end of the tube and whether ignition is produced by a flame, spark, detonator, shock wave or by some other means.

Therefore, the speed with which a detonation wave propagates is a physical constant of the particular gas mixture. It should be noted, however, that the period of combustion immediately preceding the establishment of the detonation wave is markedly influenced by many factors such as initial pressure, temperature, condition of the interior surface of the tube, diameter of the tube, composition of the mixture or method of ignition.

Theories **of the** Detonation Wave.—Betthelot and Vieille compared the speed of a detonation wave to the mean kinetic velocity of the molecules in the burned gases. This can be computed readily from the temperature attained in the combustion, but in many instances the speed thus calculated differs widely from the experimentally determined velocity of the detonation wave.

Dixon identified the speed of the detonation wave in gas mixtures with the velocity of propagation of sound at the high temperature created by the combustion. Although, for some cases, the calculated velocities agree with those actually found, for others they differ rather widely. It was soon recognized that the "sound-wave theory" was defective and inadequate.[9]

Very recently, Lewis[10] has developed a theory of the propagation by means of reaction chains. The complete reaction consists of a number of steps. The product of any one step is shot forward with a velocity corresponding to the energy of translation acquired by it and it then becomes a reactant in the next step. A similar active product or "carrier" is continually regenerated. The velocity of the "carrier" is shown to increase to a constant value, which is identified with the velocity of the detonation wave in the appropriate mixture. Consider, for example, a series of explosive mixtures of hydrogen and oxygen. It is found experimentally that the velocity of the detonation wave depends upon the concentrations of

[9] H. B. Dixon, *J. Chem. Soc.*, 97, 665 (1910).

[10] Bernard Lewis, THIS JOURNAL, 52, 3120 (1930).

hydrogen and oxygen and reaches a maximum value for a certain optimum composition, $8H_2 + O_2$. The final velocity of the "carrier" as computed by the chain-reaction theory is compared with the velocity of the detonation wave in this mixture of optimum composition. The calculated values agree very well with those found experimentally for a considerable number of different explosive mixtures. Although this picturization of the molecular mechanism in reaction chains is a step in advance, it is not easy to predict quantitatively velocities slower than that corresponding to the optimum composition mentioned above. This theory is, therefore, not to be regarded as complete, but rather as an attempt to visualize the chemical reactions occurring in the detonation wave.

A widely applicable theory was developed independently by Chapman[11] and Jouguet.[12] This theory is essentially hydrodynamical and furnishes no satisfactory explanation of the extreme rapidity with which chemical reactions occur in gaseous explosions. It would seem that a fusion of the chain reaction and the Chapman–Jouguet theories is necessary for an understanding of two striking phenomena in explosions. These are (1) the extreme rapidity of chemical reaction in the wave front, and (2) the high speed of the detonation wave. The view is held[10,13] generally that explosive reactions occur in a series of chains in which an active product of one reaction is continually used and regenerated in succeeding reactions. The chain-reaction theory is able to account rather generally for very high rates of chemical reaction.[13] Granted a high rate of chemical reaction, the Chapman–Jouguet theory is able to predict the velocity of the detonation wave. In this fusion of the two theories it is only necessary to find a "carrier" in a reaction chain that will propagate the chemical reaction through an infinitesimal element of volume in a period not greater than that required for the detonation wave to sweep across this volume. This combination of the two theories will introduce no change in the equations developed in the Chapman–Jouguet theory.

The velocities calculated by Jouguet[12] agreed reasonably well with those found experimentally. However, his more recent calculations[14] using specific heat data given by Kast, in some instances, give velocities in less satisfactory agreement with experiment than the earlier calculations.

In view of the importance of the problem of the mechanism of deto-

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[11] D. L. Chapman, *Phil. Mag.*, **47**, 90 (1899).

[12] E. Jouguet, *J. de Mathématique*, 1905, 347; 1906, 6; "Mécanique des Explosifs," Paris, 1917.

[13] C. N. Hinshelwood and co-workers, *Proc. Roy. Soc.* 1928 and 1929; N. Semenoff, *Z. Physik.*, **46**, 109 (1927); 48,571 (1928); F. Haber, and H. D. von Schweinitz, *Sitzb. preuss. Akad. Wiss.*, 1928, 499; L. Farkas, P. Goldfinger and F. Haber, *Naturwiss.*, **17**, 674 (1929); R. Mecke, *Z. physik. Chem.*, **7B**, 108 (1930); L. Farkas, F. Haber and P. Harteck, *Naturwiss.*, 12,266 (1930).

[14] E. Jouguet, *Compt. rend.*, 181,546 (1925).

nations in gases, it has seemed worth while to repeat these calculations using the best specific heat data of today and taking into account dissociation of the products. Because in this paper we deal solely with the combustion of hydrogen and oxygen mixtures, either by themselves or admixed with inert gases, the dissociations which occur to an appreciable extent at the temperatures developed and which will be considered are

$$2H_2O \rightleftharpoons 2H_2 + O_2 \quad (1)$$
$$2H_2O \rightleftharpoons H_2 + 2OH \quad (2)$$
$$H_2 \rightleftharpoons 2H \quad (3)$$

The Chapman–Jouguet Theory.—To facilitate an understanding of the method used to calculate the velocity of the detonation wave, it seems desirable to give a brief account of the Chapman–Jouguet theory.[15] Consider a plane explosion wave traveling in a tube with velocity V. The coordinate axes will be assumed to move with the wave front, which is consequently stationary in this coördinate system. AB and CD in Fig. 1 are two planes immediately ahead of and behind the wave front. Let p_1, v_1, T_1, u_1 and E_1 be the pressure, specific volume, absolute temperature, velocity with respect to the moving coördinate system, and specific internal energy of the unburned gases, respectively; and p_2, v_2, T_2, u_2 and E_2 the corresponding quantities for the burned gases. Since it is assumed that the unburned gases are at rest in a stationary system of coordinates, $u_1 = -V$. The experimental results indicate that the detonation wave is of permanent type. Assuming that this is the case, it is immediately possible to write the following three equations which state that the mass, momentum and energy of the matter contained between the planes AB and CD do not change with time

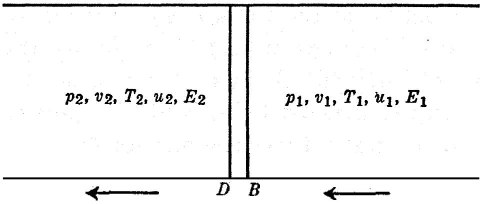

Fig. 1.—Diagram illustrating detonation wave front.

$$\text{Mass} \qquad \frac{u_1}{v_1} = \frac{u_2}{v_2} \quad (1)$$
$$\text{Momentum} \qquad \frac{u_1^2}{v_1} + p_1 = \frac{u_2^2}{v_2} + p_2 \quad (2)$$
$$\text{Energy} \qquad E_1 + \frac{u_1^2}{2} + p_1v_1 = E_2 + \frac{u_2^2}{2} + p_2v_2 \quad (3)$$

It will be initially assumed also that the chemical reaction proceeds to completion and that the composition of the burned gases is consequently

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[15] In view of the equivalence of the relations developed by Chapman and Jouguet. it seems preferable to refer to the Chapman–Jouguet theory rather than the Jouguet theory, even though Chapman's investigations are less comprehensive, An excellent account of this theory is given by R. Becker, Z. *Physik*, 8,321 (1922).

known. This furnishes the value of n_2, the number of moles per gram to be used in the equation of state

$$p_2v_2 = n_2RT_2 \tag{4}$$

These four equations give four relations between the five unknowns, V (or $-u_1$), u_2, v_2, p_2 and T_2, and an additional relation is consequently needed for their complete determination. Considerations based on mechanics and thermodynamics led jouguet to the conclusion that the required relation is

$$\frac{p_2 - p_1}{v_1 - v_2} = -\left(\frac{\partial p_2}{\partial v_2}\right)_{\text{ad}} \tag{5}$$

The additional relation which was obtained by Chapman from different considerations has been shown to be equivalent to this.

If it is assumed that the internal energy of the burned gases is a function of the temperature only, it follows that

$$E_2 - E_1 = \bar{c}_v(T_2 - T_1) - Q \tag{6}$$

where $\bar{c}_v$ is the mean specific heat of the burned gases between T_2 and T_1 and Q is the heat liberated by the reaction at constant volume, per gram of the explosive mixture. Also

$$\left(\frac{\partial p_2}{\partial v_2}\right)_{\text{ad}} = -\frac{\gamma_2 p_2}{v_2} \tag{7}$$

where γ_2 is the ratio of the specific heats for the burned gases at the temperature T_2. If

$$\mu = \frac{v_1}{v_2} \tag{8}$$

the equations given can be transformed to the forms

$$\mu^2 - \left(1 + \frac{1}{\gamma_2}\right)\mu + \frac{n_1T_1}{n_2T_2\gamma_2} = 0 \tag{9}$$

$$\bar{c}_v(T_2 - T_1) - Q - \frac{R}{2}(\mu - 1)\left(n_2T_2 + \frac{n_1T_1}{\mu}\right) = 0 \tag{10}$$

$$V = \mu\sqrt{\gamma_2 n_2RT_2} \tag{11}$$

$$\frac{p_2}{p_1} = \mu\frac{n_2T_2}{n_1T_1} \tag{12}$$

It will be seen that Equation 11 states that the velocity of the detonation wave is μ times the velocity of sound in the burned gases.

For the computation of V in the case of no dissociation, it is assumed that the combination of hydrogen and oxygen to form water vapor proceeds to completion. A value for T_2 is assumed and γ_2 for this temperature is calculated from the specific heats of the burned gas. These values for T_2 and γ_2, together with the known values of n_1, n_2 and T_1, are substituted in Equation 9, which is solved for μ. This value of μ is introduced in Equation 10, which is then solved to give an improved value of T_2. The calculations are repeated until values of μ and T_2 are found which satisfy both (9) and (10). The velocity of the detonation wave can then be found from (11) and the pressure, p_2, from (12).

The velocities for detonation waves were also calculated on the assumption that the chemical composition of the burned gases corresponds to equilibrium at the temperature and pressure attained in the wave front. The dissociation of water vapor into hydrogen and oxygen and into hydrogen and hydroxyl, and the dissociation of molecular into atomic hydrogen were considered.

Three additional variables are required to specify the chemical composition of the burned gases and three more equations are furnished by the conditions of equilibrium. By an extension of the method[16] of calculation outlined above, values for T_2, μ and the three variables which specify the composition of the burned gases are found which satisfy Equations 9 and 10 and the three conditions of equilibrium. These values can then be used to determine the velocity from Equation 11.

Two interpretations of $(\partial p_2/\partial v_2)_{ad}$ are possible when dissociation is considered. In the first, $(\partial p_2/\partial v_2)_{ad}$ is taken to mean the adiabatic change of pressure divided by change of volume for a gas of the invariable chemical composition found from the conditions of equilibrium. This interpretation leaves unchanged the equations which have been given and is the one which has been used for the calculation of velocities. The other interpretation is that $(\partial p_2/\partial v_2)_{ad}$ is to be taken on the assumption that the chemical composition of the gas changes during the adiabatic compression, so as to be in chemical equilibrium at all stages of the infinitesimal compression.

Consideration of the theory indicates that the second assumption is the one which should be used. The equations which have been given are valid for the first assumption; consequently, a strict interpretation of the theory requires that they be suitably modified in order to be in agreement with the second interpretation of $(\partial p_2/\partial v_2)_{ad}$. We have therefore calculated the velocity of detonation in a mixture of $2H_2 + O_2$ and in mixtures of $2H_2 + O_2$ diluted with six moles of hydrogen or five moles of oxygen, nitrogen, helium or argon, in two different ways. In one we have used the equations that are valid for the first interpretation of $(\partial p_2/\partial v_2)_{ad}$, and in the other, the equations that are valid for the second interpretation. In all these cases the differences between the velocities calculated in these two ways are less than 0.4%. We have therefore made all the other calculations using the first interpretation, because it is much simpler mathematically.

Choice of Data.—Eastman[17] has made an exhaustive critical study of the existing data on the specific heats of gases at high temperatures. The experimental data for diatomic gases are on the whole reasonably satisfactory up to 3000°K. As the calculated temperatures in the detonation

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[16] Lack of space prevents a detailed description of the method used for dealing with the three-fold dissociation. It may prove desirable to treat this separately in another place.

[17] E. D. Eastman, Tech. Paper 445, U. S. Bureau of Mines, 1929.

wave are often considerably in excess of this temperature a certain amount of extrapolation is necessary. The final equations which we have adapted for the specific heats of hydrogen, oxygen and nitrogen were formulated on the basis that the specific heats at constant volume reach a value of 7 at 3000°K. and remain constant thereafter. The equations used in this investigation are

$$C_{v_{H_2}} = 4.65 + 0.492 \times 10^{-3}T + 0.319 \times 10^{-6}T^2 - 0.074 \times 10^{-9}T^3$$
$$C_{v_{N_2 \text{ or } O_2}} = 4.74 + 0.408 \times 10^{-3}T + 0.486 \times 10^{-6}T^2 - 0.1234 \times 10^{-9}T^3$$

up to 3000°K. For higher temperatures the constant value, 7, is employed. The specific heats obtained from these formulas are in substantial agreement with those given by Eastman's equations.

The experimental data on the specific heat of water vapor at high temperatures are not in as satisfactory a condition. Eastman has made this the subject of a special study and has kindly sent us a copy of his unpublished manuscript. His new equation follows closely the best experimental data up to about 2700°K., reaches a maximum for C_v of 12.18 at 2800°K., and then falls off slowly at higher temperatures. There is no experimental or theoretical basis for the falling off of specific heats at high temperatures. Furthermore, Wohl and von Elbe[18] have made a few new determinations which agree with Pier's results on which Eastman's formula is based mainly, but their numerical values do not agree with Eastman's, due to different considerations in the calculations. There is every indication that the specific heat approaches an asymptotic value. We have, therefore, adopted Eastman's formula and assumed that the maximum value reached at 2800°K. remains constant at higher temperatures. The formula is

$$C_{v_{H_2O}} = 6.33 - 6.53 \times 10^{-4}T + 2.70 \times 10^{-6}T^2 - 6.145 \times 10^{-10}T^3$$

The values for the heat content of water vapor calculated from this equation agree to within less than 6% with the values given by Wohl and von Elbe for temperature up to 5000°K.

Equilibrium Constants.—The equilibrium constant for the dissociation of water vapor into hydrogen and oxygen was recalculated, using the specific heat data given above. The free energy of water vapor has been calculated by several methods by Eastman.[19] His average value at 298°K. is $\Delta F_{298} = -54{,}467$ Cal. The heat of formation of water is $\Delta H_{291} = -57{,}826$ Cal.[20]

Three equations are necessary to cover this temperature range because of the form of the specific heat equations. The final equations used are

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[18] K. Wohl and G. von Elbe, *Z. physik. Chem.*, 5B, 241 (1929).

[19] E. D. Eastman, Information Circular 6125, U. S. Bureau of Mines, 1929.

[20] "International Critical Tables," Vol. V, 1929, p. 176. The minus sign represents the evolution of energy.

Valid up to 2800°K.

$$\log K_{H_2O} = +\frac{57,295}{4.573T} - 0.848 \log T - 1.474 \times 10^{-4}T + 7.78 \times 10^{-8}T^2 - 8.72 \times 10^{-12}T^3 + 0.0616$$

Valid between 2800 and 3000°K.

$$\log K_{H_2O} = \frac{14,412}{T} + 2.0975 \log T - 7.610 \times 10^{-5}T - 2.047 \times 10^{-8}T^2 + 2.473 \times 10^{-12}T^3 - 10.4417$$

Valid above 3000°K.

$$\log K_{H_2O} = \frac{13317.3}{T} + 0.34492 \log T - 4.3285$$

The following data have been used to calculate the equilibrium constant for the dissociation of molecular into atomic hydrogen; entropy,[21] $S_{H_2\ (298)} = 31.25$; $S_{H\ (298)} = 27.4$; and $\Delta H_{298} = 103{,}500$ cal.[22]

The following equations are obtained from these data

Valid up to 3000°K.

$$\log K_{H_2} = -\frac{102,534}{4.573T} + 1.673 \log T - 0.5375 \times 10^{-4}T - 1.16 \times 10^{-8}T^2 + 1.350 \times 10^{-12}T^3 + 0.322$$

Valid above 3000°K.

$$\log K_{H_2} = 6.1622 - \frac{23,179}{T} + 0.4885 \log \frac{T}{3000}$$

An equation expressing the equilibrium constants for the dissociation of water vapor into H_2 and OH has been given by Wohl and von Elbe[18] and has been adopted here. F in the following equation is the Einstein function for the free energy of an harmonic oscillator. The figures in brackets are the values of $(h/k)\nu = \beta\nu$ calculated from the frequency of the absorption maxima in the infra-red.[23]

$$\log K_{OH} = -\frac{128,000}{4.573T} + 2.5 \log T + \frac{1}{4.573T}\,[F(6140) + 2F(5100) - 2(F(2280) + 2F(5330))] - 0.44$$

Wohl and von Elbe's equation has not been modified to conform with the specific heats used in this investigation because of the uncertainty in the heat of decomposition into OH and H_2.

It is to be emphasized that the specific heat data used in this investigation have not been calculated from the observed velocities of detonation waves, as was done by Chapman. If specific heats obtained in this way are used, it is to be expected that the calculated and observed velocities will be in close agreement. Our data have been derived from the independent sources mentioned above. Hence, the close agreement which we have found (see below) between the calculated and observed velocities for a number of explosive mixtures would seem to substantiate both the Chapman–Jouguet theory and the specific heat data used.

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[21] These are unpublished values of Giauque, and were given to us through Dr. Eastman.

[22] F. R. Bichowsky and L. C. Copeland, THIS JOURNAL, *50*, 1315 (1928).

[23] Landolt–Börnstein, fifth edition, first supplementary volume, pp. 702–704.

Results of the Calculation.—Tables I, II and III show a comparison between the calculated and experimental values. The first column contains the explosive mixture obtained by adding the indicated number of moles of gas to a stoichiometric mixture of hydrogen and oxygen—namely,

TABLE I

CALCULATED AND EXPERIMENTAL VELOCITIES OF DETONATION WAVE IN HYDROGEN AND OXYGEN DILUTED WITH NITROGEN

Explosive mixture	Calculated velocity Without dissocn., m./sec.	Calculated velocity With threefold dissocn., m./sec.	Experimental velocity, m./sec.	Deviation, %
$2H_2 + O_2$	3278	2806	2819	-0.43
$+ 1N_2$	2712	2378	2407	– 1.2
$+ 3N_2$	2194	2033	2055	-1.07
$+ 5N_2$	1927	1850	1822	+1.15

TABLE II

CALCULATED AND EXPERIMENTAL VELOCITIES OF DETONATION WAVE IN HYDROGEN AND OXYGEN DILUTED WITH OXYGEN

Explosive mixture	Calculated velocity Without dissocn., m./sec.	Calculated velocity With threefold dissocn., m./sec.	Experimental velocity. m./sec.	Deviation, %
$2H_2 + O_2$	3278	2806	2819	−0.43
$+ 1O_2$	2630	2302	2319	−0.73
$+ 3O_2$	2092	1925	1922	+0.16
$+ 5O_2$	1825	1735	1700	+2.06

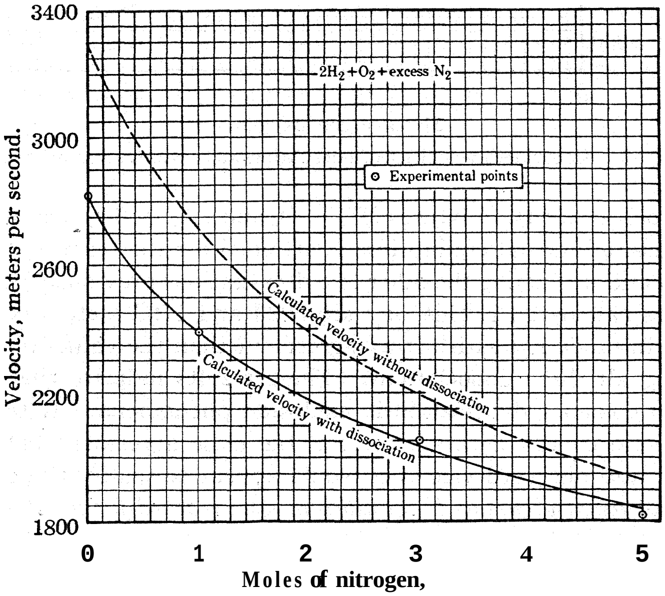

Fig. %.—Calculated velocities of detonation wave with excess nitrogen.

$2H_2 + O_2$. The second column contains the calculated velocity assuming that no dissociation occurs in the detonation wave. The third column contains the calculated velocity assuming three-fold dissociation as given above. The fourth column gives the experimental velocity determined by Dixon and others.[24] The fifth column gives the percentage deviation of the values in the third column from the experimental values.

Figures 2 and 3 show the data graphically. The circles represent the experimental points. It is seen that the agreement with the theory is exceptionally good.

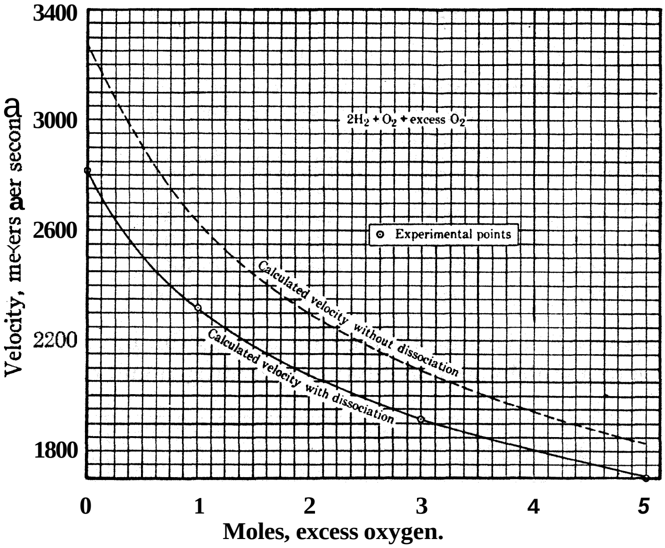

Fig. 3.—Calculated velocities of detonation wave with excess oxygen.

The velocities for the mixtures $2H_2 + O_2$ and $2H_2 + 6O_2$ were also calculated by assuming that equilibrium is attained for the reaction $2H_2 + O_2 \rightleftharpoons 2H_2O$ and neglecting the other two dissociations previously considered. The values calculated in this way are 3023 and 1793 meters per second, which are in much less satisfactory agreement than the values obtained by considering all three dissociations. These results indicate that it is important to consider dissociation in explosion phenomena. If the specific heat and free energy data are correct, the close agreement between the calculated and observed velocities would appear to justify the conclusion that *the explosion occurs as if equilibrium were reached for the three dissociations we have used.*

Table III and Fig. 4 show the results with excess hydrogen.

The agreement in the case of a large excess of hydrogen is not quite as

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[24] See Bone and Townend, "Flame and Combustion in Gases," 1927, pp. 511–518.

TABLE III

CALCULATED AND EXPERIMENTAL VELOCITIES OF DETONATION WAVE IN HYDROGEN AND OXYGEN DILUTED WITH HYDROGEN

Explosive mixture	Calculated velocity Without dissocn., m./sec.	Calculated velocity With threefold dissocn., m./sec.	Experimental velocity, m./sec.	Deviation, %
$2H_2 + O_2$	3278	2806	2819	−0.43
$+ 2H_2$	3650	3354	3273	+2.48
$+ 4H_2$	3769	3627	3527	+2.83
$+ 6H_2$	3802	3749	3532	+6.15

good. There are several possible reasons for this discrepancy. The experimental values for the mixtures with a large amount of excess hydrogen may be somewhat low. On the other hand, dissociation is almost negligible for these mixtures if equilibrium is assumed. It is quite possible that complete combustion is not realized in the wave front at these high speeds. If this is the case, the calculated values would be lower and more nearly in agreement with the observed. The incompleteness of the reaction may easily be enough to account for the difference. That there is incomplete reaction in the wave front is borne out by some direct photographs we have taken of the explosion with excess hydrogen. The photographs indicate a fair amount of combustion occurring behind the wave front, although not nearly as much as in an explosion of a $2H_2 + 1O_2$ mixture where the equilibrium falls far short of complete reaction.

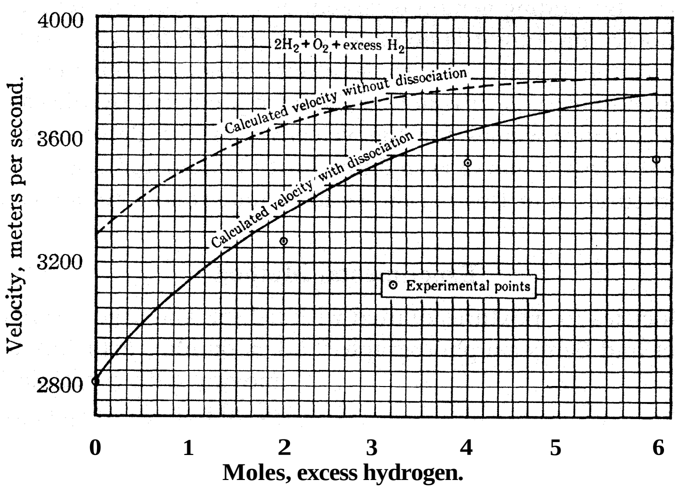

Fig. 4.—Calculated velocities of detonation wave with excess hydrogen.

The Effect of Helium and Argon.—The addition of helium and argon to the explosive mixture furnishes another means of checking the correctness of the Chapman–Jouguet theory. The theory indicates that the velocity of the detonation wave is proportional to the density of the gas mixture after combustion and to the absolute temperature reached in the wave front. If the inert gas helium be added to a mixture of $2H_2$ and $1O_2$, the velocity should increase as a result of the decreased density. On the other hand, argon, because of its greater density, should be expected to effect a decrease in the velocity. We have here the ordinarily unexpected result that two inert monatomic gases differing in atomic weight but identical in every chemical respect affect the velocity of the explosion in opposite directions. For the same quantities of added inert gas, the degree of dissociation and the heat capacities, and consequently T_2, γ_2 and μ, are the same. The calculated velocities for mixtures with an equal number of moles of helium and argon are therefore inversely proportional to the square root of the density of the burned gases.

To test the theory it is highly desirable to eliminate all variable factors except one. By adding helium or argon, or mixtures of helium and argon, to the explosive mixture it is possible to keep all factors constant with the exception of the density and to determine whether the dependence of velocity upon density is, or is not, of the form predicted by the theory.

No experimental values for the velocities of the detonation wave in mixtures of hydrogen and oxygen diluted with helium and argon were found in the literature. For this reason we have undertaken to determine their velocities.

Experimental Method

The velocities for mixtures diluted with helium and argon were obtained from direct and Schlieren photographs[25] taken on films attached to a drum moving with a peripheral speed of about 60 meters a second. Figure 5 is a sketch of the arrangement for the direct photographs. The explosion tube consisted of a thick-walled lead tube with an inside diameter of 19 mm. and of sufficient length to insure setting up the detonation wave of constant velocity. This was joined to a heavy pyrex glass tube of the same bore for the direct photographs and to a steel tube with a slit covered by a cellophane window for the Schlieren photographs. Both ends were closed by rubber stoppers which subsequently were blown out by the force of the explosion. An explosion traveling with constant velocity produces an inclined straight line on the film. The velocity of the detonation wave can be readily computed from the slope of this line, the speed of the drum and the constants of the optical arrangement.

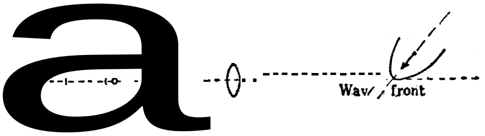

Fig. 5.—Apparatus for obtaining direct photographs of detonation waves.

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[25] Töpler, *Wid. Ann.*, 131, 33 (1867).

The gases were taken from cylinders and mixed over water. The hydrogen and oxygen were of a high degree of purity, while the helium and argon contained (by analysis) 2.95 and 4.65% nitrogen, respectively, and no combustible gases, carbon dioxide or oxygen.

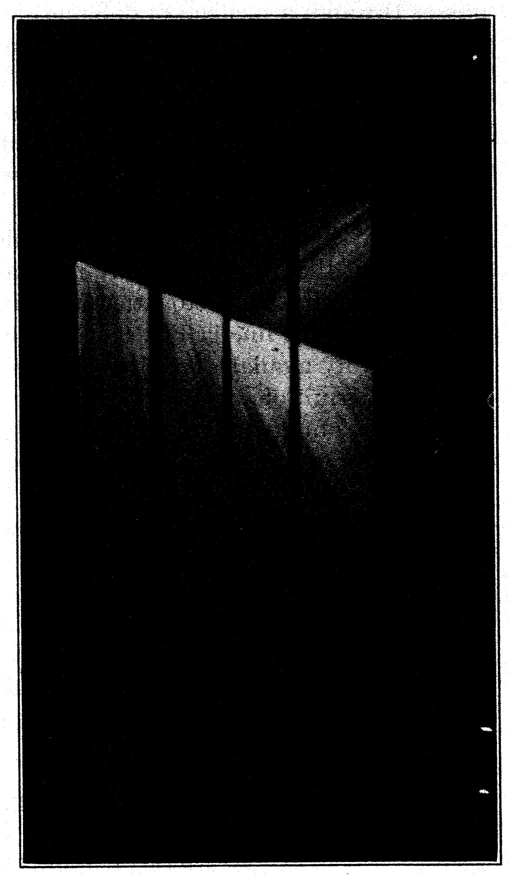

Fig. 6.—Photograph of explosion.

Figure 6 is a reproduction of a typical direct photograph. The dark vertical lines are due to strips of opaque paper placed at certain distances on the explosion tube. The upper inclined straight line represents the movement of the wave front. The lower straight line sloping in the opposite direction represents the wave reflected from the end of the tube. This travels with a reduced velocity in the partly burned medium. The photograph is an interesting one, for it can be used to give an estimate of the velocity of the gases in the rear of the wave. This velocity is obtained from the slope of the striations close to the upper straight line. Although the slope of the striations cannot be measured accurately because of its rapid rate of change, the value found for the velocity of the burned gases agrees reasonably well with the value calculated from the Chapman–Jouguet theory. The theoretical value for the velocity of the burned gases in a fixed coordinate system is

$$D = V - u_2 = \frac{\mu - 1}{} V$$

The passage of the reflected detonation wave causes more intense combustion in the burning gases. The directions of the wave and the burned gases are completely reversed. It will be observed that near the point where the reflection occurs, the velocity of the gases emitted from the reflected wave are nearly zero, due to the balancing effect of velocity of the gases from the original wave traveling in the opposite direction; but as the reflected wave meets gases with smaller and smaller velocities, the velocity of the gases emitted from it increases, as is clearly shown in the photograph. Here again the velocity of the gases falls off with time.

The Schlieren method depends upon the refraction of a beam of light as it passes through a medium of different density. The alteration of the density in the wave front is sufficient to change the direction of the beam from an arc lamp, causing it to enter the camera instead of impinging on a diaphragm. Schlieren photography has been used by W. Payman and his associates[26] in explosion experiments and will not be described in detail here. A steel tube was used, a narrow slit being cut at one end for a length of about 33 cm. to permit passage of the beam of light. The slit was covered with a cellophane window which was strong enough to remain intact until the detonation wave had passed.

The velocity of the detonation wave is determined from the slope of the inclined straight line in Fig. 6. The slopes obtained with the apparatus found readily available were not great enough, especially for the fast mixtures, to permit of any great precision in the determination of the velocity. The values obtained for a stoichiometric mixture of hydrogen and oxygen and also for mixtures containing excess oxygen and excess hydrogen are somewhat lower than those given in the literature. For this reason the results about to be given are to be considered preliminary in character and too great weight should not be attached to the lack of agreement between the calculated and observed velocities for mixtures diluted with helium and argon. With certain changes in technique that are contemplated, better experimental values can be obtained.

The experimental results in Table IV are an average of the velocities determined by both methods. They are compared with the calculated velocities with and without dissociation.

TABLE IV

CALCULATED AND EXPERIMENTAL VELOCITIES OF DETONATION WAVE IN HYDROGEN AND OXYGEN DILUTED WITH HELIUM AND ARGON

Explosive mixture	Calculated velocity Without dissocn., m./sec.	With threefold dissocn., m./sec.	Experimental velocity, m./sec.	Deviation, %
$2H_2 + O_2 + 1.5$ He	3772	3200	3010	+6.2
+ 3 He	3990	3432	3130	+9.65
+ 5 He	4083	3613	3160	+14.45
+ (2.82 He + 1.18 A)	3012	2620	2390	+9.62
+ (1.5 He + 1.5 A)	2741	2356	2330	+1.12
+ 1.5 A	2500	2117	1950	+8.45
+ 3 A	2212	1907	1800	+6.12
+ 5 A	1992	1762	1700	+3.95

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[26] Payman and Robinson, Safety in Mines Research Board Paper No. 18; Payman and Shepherd, *ibid.*, Paper No. 29. Payman, *Proc. Roy. Soc.* (London), 120A, 90 (1928).

It is observed that the predictions of the theory are verified qualitatively. In view of the preliminary nature of the experimental results this is perhaps all that could be expected. It is interesting to note, however, that the differences are in such a direction as to be accounted for by failure to attain equilibrium in the wave front. As more inert gas is added the dissociation is repressed owing to the lower temperature in the explosion. This effect is not as marked as it is with excess hydrogen, but it is possible that the presence of a large amount of inert gas prevents the attainment of equilibrium in the wave front, especially for those mixtures that possess a high velocity.

Acknowledgment.—The writers wish to acknowledge with pleasure their appreciation to W. C. F. Shepherd, investigator from the Safety in Mines Research Board, Great Britain, for his aid in taking these photographs and to D. B. Gawthrop for permission to use the Schlieren apparatus constructed by him and W. Payman of the Safety in Mines Research Board.

Summary

1. Velocities for the detonation wave in explosive mixtures of hydrogen and oxygen diluted with several gases have been calculated on the basis of the Chapman–Jouguet theory. Velocities have been computed for each of the two following assumptions: (a) the composition of the burned gases corresponds to complete combustion; (b) the composition of the burned gases corresponds to chemical equilibrium for the dissociation of water vapor into hydrogen and oxygen, and into hydrogen and hydroxyl, and for the dissociation of molecular into atomic hydrogen.
2. The calculated values for mixtures diluted with nitrogen and oxygen agree exceptionally well with the experimental values when dissociation is considered.
3. The calculated values for mixtures diluted with hydrogen are in good agreement for amounts of excess hydrogen up to four moles, but about 6% high for 6 moles of excess hydrogen. Possible reasons for the difference are suggested.
4. These results indicate the importance of dissociation phenomena in explosions.
5. The satisfactory agreement for these mixtures suggests further tests of the Chapman–Jouguet theory for mixtures diluted with helium and argon.
6. Direct and Schlieren photographs have been taken for mixtures containing various amounts of these inert gases, and the velocity of the detonation wave has been determined from them.
7. There is less satisfactory agreement with the theory than for the other mixtures. Although the predictions of the theory are verified qualitatively, the average difference between observed and calculated velocities

is about 8%. At least a part of this difference may be due to experimental error.

8. Further work is contemplated to obtain better experimental results.

PITTSBURGH, PENNSYLVANIA

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

QUENCHING OF THE FLUORESCENCE OF NITROGEN DIOXIDE

BY WARREN P. BAXTER[1]

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Of late the photochemical decomposition of nitrogen dioxide into nitric oxide and oxygen has been the object of several investigations.[2] That the absorption spectrum of nitrogen dioxide in the visible and near ultraviolet regions of the spectrum is discrete is well known.[3] Recently, Mecke[4] and Henri[5] have noted that predissociation occurs in this gas, the bands first becoming diffuse between 3800 and 3700 Å. The light absorption process in this region corresponds to the beginning of formation of an excited molecule followed by immediate dissociation into nitric oxide and oxygen. Fluorescence is to be expected in nitrogen dioxide at sufficiently low pressures when one illuminates with wave lengths above the limit of predissociation. Indeed, due to the ineffectiveness of blue light, 4358 Å., in causing photodecomposition, Norrish was led to conclude that all of this light must be reradiated. Norrish[6] succeeded in obtaining the expected fluorescence which appears as a faint yellowish luminescence when nitrogen dioxide is illuminated with the 4358 and 4047 Å. lines of the mercury arc. The spectra emitted are identical under excitation by either λ4358 or 4047, consisting of two wide maxima at 6400 and 5900 Å., except that the intensity of the 5900 band is relatively more intense with the shorter wave length. With λ3660 there is only an extremely feeble fluorescence, also in this same region. The almost complete absence of fluorescence by this light is indeed in keeping with the idea that immediately after light absorption, dissociation of the excited molecule takes place.

The object of the present investigation is the study of the intensity of the fluorescence as a function of the pressure both of nitrogen dioxide itself and of added gases. Such measurements afford quantitative data concerning the efficiencies of deactivating collisions, quantities of considerable importance in chemical kinetics.

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[1] National Research Fellow in Chemistry.

[2] Norrish, *J. Chem. Soc.*, 761 (1927); Dickinson and Baxter, THIS JOURNAL, 50, 774 (1928); Norrish, *J. Chem. Soc.*, 1158, 1604, 1611 (1929).

[3] Harris. *Proc. Nat. Acad. Sci.*, 14, 690 (1928).

[4] Mecke, *Naturwissenschaften*, 17, 996 (1929); *Z. physik. Chem.*, 7B, 108 (1930).

[5] Henri, *Nature*, 125, 202 (1930).

[6] Norrish, *J. Chem. Soc.*, 1611 (1929).

Experimental Arrangement

The fluorescence vessel was a pyrex tube, 4 cm. in diameter, with a fused-on plane end window and a side tube for applying liquid air. Connection was made through a stopcock to a reservoir of known volume (213.1 cc.) which led through a second cock to a liquid-air trap and a device for magnetically breaking small bulbs filled with nitrogen dioxide at a known pressure, and finally through another stopcock to a liquid-air trap and mercury diffusion pump. The method of introducing nitrogen dioxide was essentially that used previously.[7] The volume of the fluorescence vessel was 109.3 cc. Thus, once the fluorescence vessel had been filled with a known amount of nitrogen dioxide, the pressure could be reduced in definite steps by expansion into the evacuated reservoir. In this manner a complete set of runs could be made on a single sample of gas over the desired pressure range. Other gases (H_2, N_2, O_2, CO_2) were added from a bulb containing them through a stopcock buret. These gases were taken directly from tanks and purified by drying over phosphorus pentoxide.

The light source was a mercury arc run at atmospheric pressure. After the light had passed through suitable filters, it was collimated by lenses and diaphragms before entering the window of the fluorescence vessel. In order to observe the rather feeble fluorescence it was necessary to enclose the arc and completely darken the room

The intensity of the fluorescence was determined by a method of visual photometry. A beam of light from a small filament passed through two Nicol prisms, one of which could be rotated, and struck a small piece of cardboard placed between the eye of the observer and the path of the irradiating light as outlined by the fluorescence. The point in the beam at which the comparison of intensities was made was 3 cm. from the window the light entered. A yellow filter cut out the small amount of scattered blue and violet light. With this simple photometer it was found possible to obtain quite reproducible matches; an average of at least five settings was taken as representing a fairly accurate measure of the intensity of the fluorescence.

Fluorescence in Pure Nitrogen Dioxide.—When nitrogen dioxide is illuminated with λ4358 or 4047 Å., the incident beam is clearly outlined when viewed at right angles. The fluorescent light appears nearly white or slightly yellowish. No fluorescence was observable when illumination was made with λ3660.

In Table I are given the experimental results on the relative intensities of the fluorescence in pure nitrogen dioxide for the pressures investigated. Illumination was made with the λ4358 and 4047 lines of the mercury arc, used together to secure sufficient intensity. In the first two columns are given the pressures of nitrogen dioxide and nitrogen tetroxide, in the third the observed intensity. The fourth column gives the fractional transmission of light through the 3-cm. layer of nitrogen dioxide up to the point of observation. This was calculated for each of the pressures from Beer's law, $I = I_0e^{-\alpha lp}$, with $\alpha = 0.0192$ per cm. per mm. pressure of nitrogen dioxide. The absorption coefficients of nitrogen dioxide for λ4358 and for λ4047 were obtained incidental to some photochemical experiments and are the same within a few per cent. With the aid of a spectral photometer, Beer's law was found to hold between 4.5 and 0.3 mm. pressure and should presum-

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[7] Dickinson and Baxter, THIS JOURNAL, 50,774 (1928).

ably hold down to the lowest pressures used here. For small absorption, Beer's law reduces to the form that the absorption is proportional to the pressure. Therefore, the observed intensities, divided by the transmission and by the pressure of nitrogen dioxide, give the relative intensities of the fluorescence for the same quantity of light absorbed.

TABLE I

INTENSITY OF FLUORESCENCE IN NITROGEN DIOXIDE

Illumination by 4358 and 4047 Å. lines of mercury arc

p_{NO_2}, mm.	$p_{N_2O_4}$, mm.	Observed intensity	Transmission	$I_{corrected}$	$I = \frac{I_{corr.}}{p_{NO_2}}$	$\frac{I_0}{50p_{NO_2} + 1}$
13.9	2.92	0.0625	0.449	0.139	0.0100	0.0119
5.71	0.49	.1260	.720	.175	.0307	.0289
2.13	.07	.1468	.884	.166	.0780	.0772
0.753	.009	.1600	.958	.167	.222	.215
.259	.001	.1600	.985	.162	.626	.595
.0883	..	.1282	.995	.129	1.44	1.53
.0299	..	.0974	.998	.0976	3.26	3.32
.0102	..	.0586	.999	.0586	5.75	5.50
.00345	..	.0208	1.000	.0208	6.03	7.07
.00117	..	.0102	1.000	.0102	8.72	7.85
			Run 2			
18.3	4.01	0.0499	0.349	0.143	0.0078	0.0064
7.57	0.68	.0790	.647	.122	.0161	.0156
2.84	.10	.1018	.849	.120	.0422	.0412
1.00	.01	.1023	.944	.108	.108	.116
.345	.001	.1190	.980	.122	.354	.323
.118	..	.1018	.993	.103	.873	.855
.0400	..	.0806	.998	.0808	2.02	1.97
.0136	..	.0466	.999	.0466	3.43	3.51
.00460	..	.0243	1.000	.0243	5.29	4.80
.00156	..	.0074	1.000	.0074	4.74	5.48

The excited molecule of nitrogen dioxide produced by light absorption may either fluoresce by dropping back to lower energy levels or, on collision with other molecules, enter into chemical reaction or lose its excitation energy in other ways such as degradation to heat motion. These considerations lead to the expression[8]

$$\frac{I}{I_0} = \frac{1}{\frac{\tau}{t} + 1} = \frac{1}{ap_{NO_2} + 1} \qquad (1)$$

I_0 is the intensity of the fluorescence at zero pressure, I, the intensity at the pressure p_{NO_2} and τ the natural life of the excited molecule before dropping back to a lower level. The mean time between collisions, t, is inversely proportional to the pressure and from kinetic theory has the value

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[8] Stern and Volmer, *Physik. Z.*, 20, 183 (1919).

$$t = \frac{1}{N\sigma_{12}^2(8\pi kT)^{1/2}\left(\frac{m_1 + m_2}{m_1m_2}\right)^{1/2}} \qquad (2)$$

At 25° this reduces to the numerical form

$$t = \frac{3.90 \times 10^{-23}}{p\left(\frac{M_1 + M_2}{M_1M_2}\right)^{1/2}} \qquad (3)$$

with the pressure, p, in mm. of mercury. Any efficiency factor may be included in σ_{12}, the distance between nuclei for a quenching collision. The constant a in Equation 1 is an abbreviation

$$a = 2.56 \times 10^{22}\left(\frac{M_1 + M_2}{M_1M_2}\right)^{1/2}\sigma_{12}^2\,\tau \qquad (4)$$

A plot of $1/I$ against the pressure gives a straight line with the slope a/I and intercepts $1/I_0$. Run 1 when treated in this manner gives $a = 50$ mm.$^{-1}$. Run 2 similarly results in $a = 47$. These results were checked in the following manner. Values of I_0 were calculated from Equation 1 for each observed point with assumed values of the constant a. With the correct a the set of values of I_0 so obtained should be constant over the whole range. In this manner a was found to be equal to 50 mm.$^{-1}$ for Run 1 and between 45 and 50 mm.$^{-1}$ for Run 2. One run with illumination by λ4047 alone leads to $a = 40$. This latter value is necessarily approximate, due to the difficulties attending the measurement of the feeble intensity of fluoresced light in this case. In the sixth column of Table I are given the values of I calculated from the expression

$$\frac{I}{I_0} = \frac{1}{50p_{NO_2} + 1}$$

with $I_0 = 8.3$ in Run 1 and 5.9 in Run 2. Inspection of the last two columns of the table shows that the functional relationship between the pressure of nitrogen dioxide and the intensity of fluorescence given by Equation 1 holds quantitatively over a pressure range of 12,000-fold with a corresponding variation in the intensity of 850-fold. Such agreement is confirmation of the general idea that the light first produces an excited molecule which may then fluoresce or be damped by collision.

It is evident that at a pressure of nitrogen dioxide of 0.02 mm. the fluorescence is half damped. From the experimental result $a = 50 = 5.35 \times 10^{21}\sigma_{12}^2\tau$ it follows that $\sigma_{12}^2\tau = 9.3 \times 10^{-21}$ cm.^{2} sec. If we assume τ is 10^{-7} sec., σ_{12} must be 30×10^{-8} cm. or about ten times ordinary kinetic theory diameters. On the other hand, if σ_{12} is taken equal to 3×10^{-8} cm., τ must be as long as 10^{-5} second. The lives of excited atoms, investigated by Wien[9] and Kerschbaum,[10] are all of the order of magnitude of 10^{-7} or 10^{-8} seconds. It is natural to suppose that the lives of optically

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[9] Wien, *Ann. Physik,* 83, 1 *(1927).*

[10] Kerschbaum, *ibid.,* 83, *287* (1927).

excited molecules should be of the same order of magnitude. On the other hand, it is quite common for large diameters to appear in collisions of the second kind. For example, the measurements of Stuart[11] on the quenching of the resonance fluorescence of mercury by hydrogen and carbon monoxide lead to diameters of the excited mercury atom several times that of the normal atom. Also Mannkoff[12] finds similar dimensions in the case of damping of fluorescence in sodium vapor by nitrogen and hydrogen. Kallmann and London[13] have treated on a quantum mechanical basis the problem of abnormally large effective diameters and succeeded in giving a reasonable explanation of their repeated appearance in terms, among other things, of the closeness of resonance between the two systems. Thus, depolarization by sodium vapor of the fluorescence of the D-lines of sodium[14] may occur at distances many thousand-fold ordinary kinetic theory values. Hence we may conclude that the apparently large diameters found here in the quenching of the nitrogen dioxide fluorescence by nitrogen dioxide itself are reasonable and that there is no necessity for assigning an exceptionally long life (10^{-5} second) to the optically excited nitrogen dioxide molecule.

Quenching of Fluorescence by Foreign Gases.—The addition of oxygen, hydrogen, nitrogen or carbon dioxide to the nitrogen dioxide produces a noticeable decrease in the intensity of the fluorescence. Figure 1 illustrates the quenching of the nitrogen dioxide fluorescence in the presence of oxygen. Such an effect is to be expected since in this case more collisions of the second kind should occur. In place of Equation 1 we have

$$\frac{I}{I_0} = \frac{1}{\Sigma_i \frac{\tau}{t_i} + 1} \tag{5}$$

When there is only one added gas this becomes, using the experimental result of the preceding section

$$\frac{I}{I_0} = \frac{1}{50p_{\mathrm{NO_2}} + ap + 1} \tag{6}$$

Calling J_0 the observed intensity in pure nitrogen dioxide at the pressure $p_{\mathrm{NO_2}}$, and J the intensity after the addition of the pressure, p, of foreign gas we obtain the ratio

$$\frac{J}{J_0} = \frac{p_{\mathrm{NO_2}}\,(I)_{p=p}}{p_{\mathrm{NO_2}}\,(I)_{p=0}} = \frac{50p_{\mathrm{NO_2}} + 1}{50p_{\mathrm{NO_2}} + ap + 1} = \frac{1}{cp + 1} \tag{7}$$

where $c = a/(50p_{\mathrm{NO_2}} + 1)$, a constant for any particular pressure of nitrogen dioxide.

Table II contains the experimental results on the quenching of the fluorescence by various gases. The observations are given in full for the

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[11] Stuart, *Z. Physik*, 32, 262 (1925); Gaviola, *Phys. Rev.*, 33, 309 (1929).

[12] Mannkoff, *Z. Physik*, 36, 315 (1926).

[13] Kallmann and London, *Z. physik. Chem.*, 2B, 207 (1929).

[14] Datta, *Z. Physik*, 37, 625 (1926); Hanle, *ibid.*, 41, 164 (1927).

case of nitrogen; the other gases give similar results. The values of c are indeed constant within the experimental error throughout any single run. Moreover, the values of a calculated from each run are in good accord among themselves, as seen from the last column of Table II, thus establishing the general validity of Equation 6, which relates the intensity of fluorescence to the pressure of both nitrogen dioxide itself and the foreign gas. The effect of nitrogen tetroxide has been neglected. In the preceding section this factor comes into question only at the highest pressures,

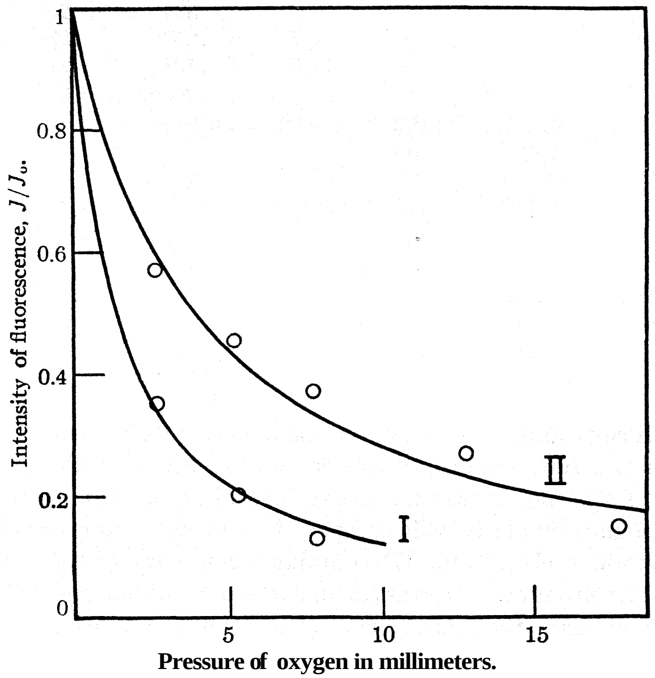

Fig. 1.—Quenching of fluorescence by oxygen. Solid curve from $\frac{J}{J_0} = \frac{1}{\frac{16.5}{50P_{\mathrm{NO}_2} + 1}\,p_{\mathrm{O}_2} + 1}$ I, P_{NO_2}, 0.436 mm.; II, P_{NO_2}, 1.256 mm.

where the observations may already be in error in the correction for light transmission. Since, however, carbon dioxide is practically as efficient in quenching as nitrogen dioxide, we might assume that nitrogen tetroxide has also the same efficiency. The pressure p_{NO_2} should then be replaced by $p_{\mathrm{NO}_2} + p_{\mathrm{N}_2\mathrm{O}_4}$. This would lead to a somewhat better check among the various values of a.

It is to be noticed that the pressure of added gas which damps the fluorescence to one-half is not an immediate measure of the life of excited

TABLE II

QUENCHING OF FLUORESCENCE BY FOREIGN GASES

Added gas	p_{NO_2}, mm.	$p_{N_2O_4}$, mm.	$p_{\text{added gas}}$, mm.	J/J_0	c, mm.$^{-1}$	a, mm.$^{-1}$
Nitrogen	0.587	0.005	2.62	0.384	0.61	
			5.21	.191	.81	
				Average	0.71	22
	1.685	0.038	2.60	0.566	0.29	
			5.17	.465	.22	
			7.70	.388	.20	
			10.2	.334	.20	
			12.7	.257	.23	
			15.2	.193	.27	
				Average	0.237	20
Hydrogen	0.378	0.002	2.62	0.211	1.43	28
	1.085	.018			0.44	24
				Average		26
Oxygen	0.436	.002			0.75	17
	1.256	.017			0.25	16
				Average		16.5
Carbon dioxide	0.857	.006			1.15	50
	.940	.010			0.98	47
	2.18	.047			.35	37
				Average		44

nitrogen dioxide and the deactivating diameter, since the ratio of observed intensities is a function also of the pressure of nitrogen dioxide. Rather the value of a is such a measure; its reciprocal gives the pressure at which the fluorescence would be half damped if there were no quenching by nitrogen dioxide itself. Table III contains a summary of the experimental results. The product, $\sigma_{12}^2\tau$, was calculated from a by means of Equation 4. Column 5 contains the relative efficiencies of the various added gases in quenching fluorescence, nitrogen dioxide arbitrarily being set equal to unity. The last column gives the value σ_{12}, the effective deactivational diameter, assuming a mean life of the excited nitrogen dioxide molecule of 10^{-7} second.

The specific nature of collisions of the second kind is shown by Table III. Carbon dioxide is practically as effective as nitrogen dioxide in quenching, while nitrogen, oxygen and hydrogen are only one-quarter or one-fifth as effective in this respect. The molecular complexity of the triatomic molecules, CO_2 and NO_2, implies a greater number of higher energy levels than is possessed by the simpler diatomic molecules. It is known that collisions of the second kind are more effective for those cases in which a small amount only of the excitation energy is to be transformed into kinetic energy. It is therefore not surprising that carbon dioxide and nitrogen dioxide are indeed the more efficient in damping fluorescence.

TABLE III

EFFICIENCY OF QUENCHING COLLISIONS

Quenching gas	a, mm.$^{-1}$	$p_{1/2}$, mm.	$\sigma_{12}^2\tau \times 10^{21}$ cm.^{2} sec.	Relative efficiency	$\sigma_{12} \times 10^8$ ($\tau = 10^{-7}$ sec.), cm.
NO_2	50	0.020	9.3	1	31
CO_2	44	.023	8.2	0.87	29
N_2	21	.048	2.7	.29	16
O_2	16.5	.061	2.2	.24	15
H_2	26	.038	1.4	.15	12

Summary

The intensity of fluorescence excited in nitrogen dioxide by the 4358 and 4047 Å. lines of the mercury arc has been determined for the pressure range 0.001 to 18 mm. Nitrogen dioxide is very efficient as a quenching agent; the fluorescence is half damped at a pressure of 0.02 mm. The product of the square of the effective diameter for collision and the life of the excited molecule $\sigma_{12}^2\tau$ is 9.3×10^{-21} cm.^{2} sec. This result indicates a deactivational diameter approximately ten times greater than kinetic theory values.

It is shown that the quenching of this fluorescence by foreign gases is in quantitative agreement with Equation 7, which is based on the occurrence of deactivating collisions with these gases as well as with nitrogen dioxide itself. There is specificity in quenching by added gases; the relative deactivational efficiencies of carbon dioxide, nitrogen, oxygen and hydrogen referred to nitrogen dioxide as unity are, respectively, 0.87, 0.29, 0.24 and 0.15.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF SASKATCHEWAN, SASKATOON, SASKATCHEWAN]

STUDIES ON THE THERMOCHEMISTRY OF THE COMPOUNDS OCCURRING IN THE SYSTEM $CaO-Al_2O_3-SiO_2$. IV. THE HEAT OF SOLUTION OF TRICALCIUM ALUMINATE AND ITS HYDRATES IN HYDROCHLORIC ACID[1]

BY T. THORVALDSON, WELDON G. BROWN AND C. R. PEAKER

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The heats of solution of the compounds occurring in the system $CaO-Al_2O_3-SiO_2$ and of their hydration products are of interest not only for the purpose of calculating the heat of formation of these compounds but also in connection with problems relating to the constitution of hydraulic cements and elucidation of the reactions which take place during their hydration. This applies especially to the aluminates and the silicates of calcium which are rich in lime. The paucity of such data is probably mainly due to the difficulty of preparing sufficient quantities of these substances in a pure

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[1] The authors wish to acknowledge generous financial assistance from the National Research Council of Canada.

state. The present paper describes the determination of the heats of solution of tricalcium aluminate and its hydrates in $HCl \cdot 20H_2O$ and $HCl \cdot 200H_2O$.

Apparatus and Experimental Procedure.—The calorimeter, which was of the Richards adiabatic type with a slight modification, the Beckmann thermometers used, the method of introducing the sample into the calorimeter aad the limits of adiabatic control have been described elsewhere.[2]

The general procedure used was to determine the heat of solution of the aluminate in $HCl \cdot 20H_2O$. The heat of dilution of $HCl \cdot 20H_2O$ and of the resulting solution of aluminate, when diluted to a concentration corresponding to $HCl \cdot 200H_2O$, was determined by the method of Richards, Rowe and Burgess,[3] and the heat of solution of the aluminate in $HCl \cdot 200H_2O$ then calculated according to the usual method.[3]

Preparation of Materials

Calcium Carbonate and Alumina.—The method of purification of the calcium carbonate was similar to that already described.[2a] The aluminum hydroxide was purified by precipitation from a boiling 2% solution of ammonia alum which was free from iron, using redistilled ammonia water; the precipitate was washed thoroughly by decantation, filtered off, washed, redissolved in pure hydrochloric acid, the solution diluted to the original volume and the precipitation as aluminum hydroxide repeated. After thorough washing, the aluminum hydroxide was dried in a covered platinum dish and ground to pass a 200-mesh sieve. The material had an ignition loss of about 30%.

Tricalcium Aluminate. Sample 1.—Calcium carbonate and aluminum hydroxide, prepared as described above, were mixed wet in the proportions $3CaO:Al_2O_3$. The water was then evaporated with constant stimng of the mixture to prevent segregation. When dry. the material was transferred to platinum crucibles, placed in a platinum-wound resistance furnace, the temperature gradually raised to 1300" and kept there for several hours. The sintered mass was then broken up, ground in an agate mortar to pass a 200-mesh sieve, and the heating repeated, the temperature being raised to about 1370°. Microscopic examination showed that even after several heat treatments at 1370" the material contained small amounts of free lime and $5CaO \cdot 3Al_2O_3$. It was found that treating the finely powdered material with water aided combination materially during the subsequent heat treatment due probably to dispersion of the free lime by hydration. The treatment, however, seemed to cause tiny voids to be formed in the crystals of tricalcium aluminate and this made exact microscopic examination more difficult. These voids were eliminated by subsequent heat treatments. The material was repeatedly ground and reheated until White's test* indicated absence of free lime. and careful examination by the petrographical microscope showed that the sample was homogeneous and free from particles of lime and $5CaO \cdot 3Al_2O_3$. It was composed of isotropic crystals, with a refractive index of 1.710 ± 0.002.

Sample 3.—Sample 3 was prepared in the same way as Sample 1. This sample, however, contained a small amount of $5CaO \cdot 3Al_2O_3$ but no free lime. Table I gives the analysis of the two samples.

(a) Thorvaldson, Brown and Peaker, THIS JOURNAL, 51, 2678 (1929); (b) Thorvaldson and Brown, *ibid.*, **52**, 80 (1930).

[3] Richards, Rowe and Burgess, *ibid.*, 32, 1176 (1910).

[4] White, *J. Ind. Eng. Chem.*, 1, 5 (1909).

TABLE I

ANALYSES OF TRICALCIUM ALUMINATE[a]

	Sample 1	Sample 3	Calcd.
Calcium oxide (CaO)	62.31	61.98	62.27
Alumina (Al_2O_3)	37.76	37.98	37.73

Ferric oxide, alumina and silica were absent from both samples.

[a] Analyses by David Wolochow.

$HCl\cdot 20H_2O$.—C. P. acid was redistilled through a partly refluxing quartz condenser, the middle portion of the distillate collected in silica flasks and adjusted to $HCl\cdot 20H_2O$, the concentration being determined both by titration with pure sodium carbonate and by gravimetric determination of chloride.

The Specific Heat of $HCl\cdot 20H_2O$

Recent determinations of the specific heat of hydrochloric acid of various concentrations by Richards, Mair and Hall[5] have given values which differ somewhat from the previously accepted ones. Unfortunately the specific heat of $HCl\cdot 20H_2O$ was not included among those redetermined. It was therefore decided to determine the specific heat of $HCl\cdot 20H_2O$ over both the temperature intervals 16 to 20 and 18 to 20°. The acid used in this determination was purified with special care and gave the composition $HCl\cdot 20.01H_2O$ by titration with sodium carbonate and $HCl\cdot 20.02H_2O$ by gravimetric analyses of chloride.

The method used for the determination of specific heat was that of Richards and Rowe.[6] The calorimeter can was of pure gold, while containers for the sulfuric acid and alkali were made of a gold alloy (80% gold and 20% copper). This alloy was not attacked appreciably during the series of experiments by the solutions in contact with it.

The concentrations of sulfuric acid and sodium hydroxide used for the series for the interval 16 to 20° were: H_2SO_4, 6.928%; NaOH, 27.73%; and for the series for the interval 18 to 20°: H_2SO_4, 4.235%; NaOH, 13.86%. As practically the same weights of the acid and alkali were used for each determination and as both the water standardization and the determinations of specific heat covered exactly the same temperature range it was not necessary to know the specific heats of these solutions with a high degree of accuracy. The following values for specific heats were used: H_2SO_4 (6.928%), 0.94; H_2SO_4 (4.235%), 0.96; NaOH (27.73%), 0.83; NaOH (13.86%), 0.87.

Tables II and III give the experimental data for the determinations over the interval 16 to 20°. In Table 11, Q_{100} represents the heat evolved during the neutralization of 100.0 g. of the solution of sulfuric acid, at 20°.

A similar series of experiments, including water standardization, was made with the same solution of hydrochloric acid over the temperature

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[5] Richards, Mair and Hall, THIS JOURNAL, 51, 727 (1929).

[6] Richards and Rowe, *Proc. Am. Acad. Arts Sci.*, 49,175 (1913).

TABLE II

WATER STANDARDIZATION

Total heat capacity, 510.3 cal./deg. Weight of water, 400.5 g. Weight of NaOH colution, 17.09 g.

Expt.	H_2SO_4 soln., g.	Final temp., °C.	Corr. rise,[a] °C.	Q_{100}, calories
1	85.116	20.01	3.989	2391.6
2	85.098	19.99	3.982	2387.9
3	85.102	19.99	3.985	2389.6
4	85.102	19.99	3.986	2390.2
5	85.102	19.99	3.985	2389.6
Mean		19.99	3.985	2389.2

TABLE III

SPECIFIC HEAT OF $HCl\cdot 20H_2O$

Heat capacity of apparatus, H_2SO_4 and NaOH, 109.8 cal./deg. Weight of $HCl\cdot 20H_2O$, 470.6 g. Weight of NaOH solution, 17.09 g.

Expt.	H_2SO_4 soln., g.	Final temp., °C.	Corr. rise,[a] °C	Specific heat[b] $HCl\cdot 20H_2O$ Mean cal. 16–20'
1	85.105	19.99	3.987	0.8505
2	85.098	20.09	3.985	.8508
3	85.115	19.96	3.988	.8507
4	85.103	20.01	3.987	.8507
5	85.320	19.99	3.986	.8512
6	85.119	19.97	3.989	.8505
Mean		20.00	3.987	.8507

[a] The temperature rise is corrected for exposed stem, setting and stirring. [b] As the average final temperature of the water standardization series was 19.99° and the temperature coefficient for the neutralization of sulfuric acid is fairly large, a small correction was applied in Expts. 2, 3, 4 and 6 of Table III for the variation in the final temperature from 19.99°. For this purpose the temperature coefficient given by Richards and Rowe[7] (—49.5 cal. per $^1/_2$ mole H_2SO_4 per °C.) and the average value for the heat of neutralization of 100 g of 6 928% H_2SO_4 obtained in Table II were used.

interval 18–20'. The value obtained for the specific heat of $HCl\cdot 20H_2O$ over this range was 0.8510 (mean calorie 18–20°).

The value 0.8507 for the specific heat of $HCl\cdot 20H_2O$ over the range 16–20° is considerably higher than the preliminary value of 0.8487 given by Richards and Rowe.[7] It may, however, be shown that our result is consistent with those of Richards, Mair and Hall[5] for more dilute solutions of hydrochloric acid by plotting the apparent molal heat capacity with the square root of the molality as Randall and Rossini[8] have done for a number of electrolytes. This provides an extremely sensitive graphical method of comparing the results (Fig. 1).

[7] Richards and Rowe, THIS JOURNAL, 42, 1621 (1920).

[8] Randall and Rossini, *ibid.*, 51, 323 (1929); Rossini, Bur. *Stands.* **J.** ***Res.*, 4,** 313 (1930).

The Heat of Solution of Tricalcium Aluminate in $HCl \cdot 20H_2O$ and in $HCl \cdot 200H_2O$

The results of the determinations of the heat of solution of tricalcium aluminate, Sample No. 1, in $HCl \cdot 20H_2O$ are given in Table IV. The specific heats used in calculating the heat capacity of the calorimeter system were: gold, 0.031; gold alloy (80% Au, 20% Cu), 0.44; $HCl \cdot 20H_2O$ (16–20°), 0.8507, (18–20°), 0.8510. The specific heat for $HCl \cdot 20H_2O$ is in terms of the specific heat of water over the same temperature interval. All weights were corrected to vacuum.

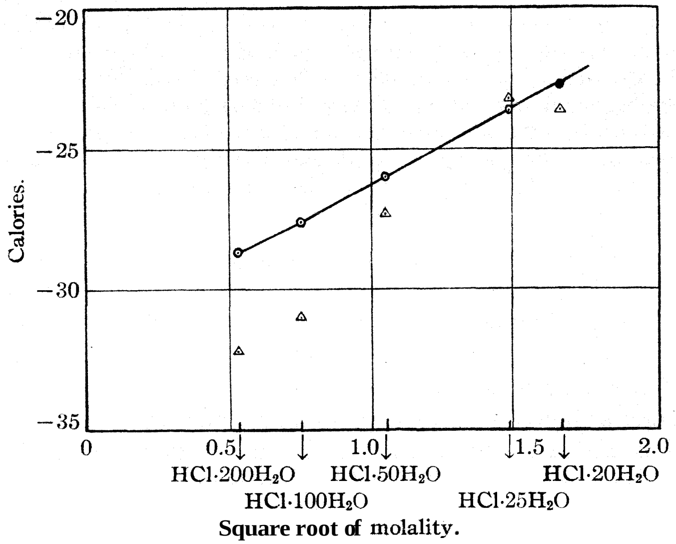

Fig. 1.—Apparent molal heat capacity of HCl at 18°. ⊙, Richards, Mair, and Hall; △, Richards and Rowe; ●, Thorvaldson, Brown and Peaker ($HCl \cdot 20H_2O$).

From Table IV one finds that the average proportion of aluminate to acid is 1 g. to 210.7 g. of $HCl \cdot 20H_2O$. In order to calculate the heat of solution of tricalcium aluminate in $HCl \cdot 200H_2O$ it is necessary to determine the heats of dilution of 210.7 g. of $HCl \cdot 20H_2O$ to $HCl \cdot 200H_2O$ and of 211.7 g. of the aluminate solution to a corresponding dilution. It is also necessary to determine the heat effect of mixing the resulting diluted solutions.

Ten determinations of the heat of dilution of $HCl \cdot 20H_2O$ to $HCl \cdot 200H_2O$ were made. The weight of $HCl \cdot 20H_2O$ used for each experiment was 61.21 g., the total heat capacity was 564 cal. and the final temperature 20.0°. The corrected rise varied from 0.150 to 0.152° with a mean of 0.1509°. The heat of dilution is therefore 85.11 calories for 61.21 g. or 293.0 calories for 210.7 g. of $HCl \cdot 20H_2O$.

In a similar way it was found that 211.7 g. of the aluminate solution gave

TABLE IV

HEAT OF SOLUTION OF $3CaO{\cdot}Al_2O_3$, SAMPLE 1, IN $HCl{\cdot}20H_2O$

Weight of $HCl{\cdot}20H_2O$, 600.4 g.

Expt.	$3CaO{\cdot}Al_2O_3$, g.	Final temp., °C.	Corr. rise,[a] °C.	Heat capacity,[c] 18° cal.	Heat of soln. per gram at 20°, cal.$_{20°}$
1	2.8481	20.01	3.968	528.6	736.8
2	2.8649	19.95	3.991	528.6	736.7
3	2.8766	19.96	4.007	528.6	736.6
4	2.8034	19.99	3.971	519.0	735.5
5	2.8558	20.05	4.041	519.0	734.7
Mean		19.99			736.1
corrected for evaporation[b]					736.4

[a] Corrected for stem exposed, setting of thermometer and stirring [b] The volume of air in the calorimeter was about 600 cc. This was no doubt saturated with water vapor at the beginning of each run and probably nearly saturated at the end of each run. Three-fourths of the calculated correction for the heat of vaporization is applied. [c] The temperature of the sample of tricalcium aluminate when introduced into the calorimeter was 20°. The heat capacity of the aluminate is therefore not included in the calculated value.

on corresponding dilution the mean value of 289.4 calories. For this determination it was necessary to know the specific heat of the aluminate solution. Determinations, made as for $HCl{\cdot}20H_2O$ described above, gave 0.847 calorie per degree and this value was not found to vary appreciably for the different aluminate solutions used.

Experiments showed that there was no heat effect produced when $HCl{\cdot}200H_2O$ was added to the diluted aluminate solution. Thus the heat of solution of $3CaO{\cdot}Al_2O_3$ in $HCl{\cdot}200H_2O$ is independent of the proportion of aluminate to acid at least for proportions approximating those used. The calculated value for the heat of solution of $3CaO{\cdot}Al_2O_3$ in $HCl{\cdot}200H_2O$ at 20° is therefore 732.8 (736.4 + 289.4 − 293.0) calories (20°) per gram.

The Heat of Solution of $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ in Hydrochloric Acid.[9]—Thorvaldson and Grace[10] have shown that tricalcium aluminate forms a very stable hydrate of the composition $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$. This hydrate is readily formed when tricalcium aluminate is hydrated in steam under pressure.

Determinations of the heat of solution of two samples of $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ prepared from $3CaO{\cdot}Al_2O_3$, Sample 1, were made. Sample A was prepared by exposing the freshly ignited aluminate to saturated steam at 150° in an autoclave and drying the resulting hydrate to constant weight over calcium oxide. It was found that the $3CaO{\cdot}Al_2O_3$ had taken up 39.97% of water, which corresponds to a formula of $3CaO{\cdot}Al_2O_3{\cdot}5.99H_2O$

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[9] The authors are indebted to Mr. Norman S. Grace for preparing the samples of the hydration products of tricalcium aluminate used in the determinations of the heat of solution.

[10] Thorvaldson and Grace, Canadian *J.* Res.. **1**, 36 (1929).

Sample B was prepared by adding water to the anhydrous aluminate and drying to constant weight over calcium oxide, this process of treating with water and drying being repeated several times. The total increase in weight after drying over lime was 40.08%, which corresponds to a formula of $3CaO·Al_2O_3·6.01H_2O$.

Special precautions were taken to prevent access of the carbon dioxide of the air to the samples during the preparation of the hydrate. This could be effectively prevented in the case of the hydrate prepared in steam by taking care that the air and water in all vessels were free from carbon dioxide. There was a somewhat greater chance in the case of the sample prepared at room temperature for contact with ordinary air and there may have been a slight absorption of carbon dioxide. This probably accounts for the slightly lower heat of solution obtained for Sample B. Both samples were entirely isotropic and had an index of refraction,'' N_{Na} 1.604 * 0.002.

TABLE V

HEAT OF SOLUTION OR $3CaO·Al_2O_3·6H_2O$ IN $HCl·20H_2O$

Total heat capacity, 519.2 cal./deg. Weight of $HCl·20H_2O$, 600.4 g.

Sample	$3CaO·Al_2O_3·6H_2O$, g.[c]	$3CaO·Al_2O_3$, g.	Final temp., °C.	Corr. rise,[a] °C.	Heat of soln.[b] at 20° cal.$_{20}$ per gram $3CaO·Al_2O_3$
A		2.0961	20.06	2.114	523.8
A		2.1417	20.09	2.145	520.2
A		2.0596	19.85	2.083	525.3
A		2.0147	19.83	2.029	523.1
Average for Sample A			19.96		523.1
B	2.8448	2.0308	20.01	2.032	519.7
B	2.8502	2.0347	19.98	2.039	520.5
Average for Sample B			19.995		520.1
Average for Samples A and B.				....	522.1

[a] Corrected for stem exposed, setting of thermometer and stirring. [b] Corrected for evaporation and from the 19° to the 20° calorie. [c] The temperature of the sample of hydrated tricalcium aluminate when introduced into the calorimeter was 20°. The heat capacity of the aluminate is therefore not included in the calculated value for heat capacity.

The heat of dilution of the aluminate solution obtained from the experiments recorded in Table V to a dilution corresponding to $HCl·200H_2O$ at 20° was determined. Four determinations gave exactly the same value, namely, 84.09 calories for the heat of dilution of 61.43 g. of the solution (that is, a temperature rise of 0.149° for a heat capacity of 564.4 cal./deg.). Considering the determinations with Sample A in Table V, the average weight of $HCl·20H_2O$ used per gram of anhydrous tricalcium aluminate was 288.9 g. and the corresponding average weight of aluminate solution pro-

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[11] Measurements by V. A. Vigfusson.

duced was 290.3 g. The heats of dilution amount to 401.7 and 397.4 calories, respectively.

The value for the heat of solution of $3CaO\cdot Al_2O_3\cdot 6H_2O$ (Sample **A)** in $HCl\cdot 200H_2O$ at 20° is therefore 518.8 $\text{calories}_{20°}$ per gram of anhydrous tricalcium aluminate or 370.6 $\text{calories}_{20°}$ per gram of the hydrate.

The calculated heat of hydration of tricalcium aluminate to the hexahydrate at 20° is 214.0 $\text{calories}_{20°}$ per gram or 57.8 kg. $\text{calories}_{20°}$ per formula weight.

Heats of Solution of Higher Hydrates of $3CaO\cdot Al_2O_3$

A crystalline hydrate of tricalcium aluminate occurring as hexagonal plates, needles and spherulites is well known. Attempts to obtain this hydrate in the pure state and determine its water of hydration have produced results which are apparently very discordant, Gallo,[12] Klein and Phillips[13] and Pulfrich and Linck[14] reporting a water content varying from 5.5 to 10.5 molecules. Later experimental work[15] has shown that special precautions must be taken in order to obtain this hydrate free from admixture of the isotropic hydrate $3CaO\cdot Al_2O_3\cdot 6H_2O$. Further, it appears that on drying, the crystalline hexagonal plates, which when formed in equilibrium with water near its freezing point probably have the composition $3CaO\cdot Al_2O_3\cdot 12H_2O$, give up their water of hydration in several steps without a material change in the crystalline form until exposure over calcium oxide produces a material of the composition $3CaO\cdot Al_2O_3\cdot 8H_2O$.

There seems, however, to be some doubt as to the existence of several anisotropic hydrates of tricalcium aluminate. It was thought that determinations of the heat of solution of hydrated material containing varying amounts of water might give an indication as to the way in which the water is held. In determining the heat of solution of calcium hydroxide in $HCl\cdot 200H_2O$ it was found[2b] that this substance is capable of taking up large quantities of water with only a very slight decrease in the heat of solution. As it is generally accepted that calcium hydroxide does not form a higher hydrate, a similar change in the heat of solution of hydrated tricalcium aluminate with increasing water content would suggest that the water is not bound chemically.

The higher hydrates of tricalcium aluminate were formed by the gradual addition of anhydrous tricalcium aluminate to carbon dioxide-free water, the mixture being cooled by ice. The hydrate was then kept in contact with water below 21° for about two weeks, after which portions were dried at 21° over saturated solutions of various salts. The method is described in detail elsewhere.[15]

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[12] Gallo, *Gazz. chim. ital.*, 38, II, 156 (1908).

[13] Klein and Phillips, Techn. Paper No. 43, U. S. Bureau of Standards, 1914.

[14] Pulfrich and Linck, *Kolloid-Z.*, 34, 117 (1924).

[15] Thorvaldson, Grace and Vigfusson, *Canadian J. Res.*, 1, 201 (1929).

The hydrates used for this series of determinations were prepared from $3CaO{\cdot}Al_2O_3$, Sample **3.** This sample is slightly low in lime and contains therefore a small quantity of the aluminate next lower in lime, namely, $5CaO{\cdot}3Al_2O_3$. On hydration this substance forms hydrated tricalcium aluminate with liberation of the excess of alumina as hydrate. It was found that the heat of solution of Sample **3** in $HCl{\cdot}200H_2O$ was 9.3 calories per gram lower than that obtained with the purer Sample No. 1, but the heat of solution of the hydrate ($3CaO{\cdot}Al_2O_3{\cdot}6H_2O$) obtained by exposing Sample No. **3** to steam under pressure was also 9.3 calories lower than that for the corresponding product from Sample 1, giving a calculated heat of hydration of 214.1 for Sample 3 against 214.0 calories for Sample 1. There was therefore good reason to expect that the *differences* in the heat of solution of the various hydrates prepared from Sample **3** would not differ materially from those which would have been obtained with hydrates from the purer Sample, No. 1. Table VI gives the calculated heats of hydration of tricalcium aluminate to hydrates containing four different amounts of water.

TABLE VI

HEAT OF HYDRATION OF TRICALCIUM ALUMINATE CALCULATED FROM VALUES FOR HEATS OF SOLUTION OF THE HYDRATES IN $HCl{\cdot}200H_2O$

Hydration of $3CaO\ Al_2O_3$	Hwt effect calories per gram of anhydrous aluminate
$3CaO{\cdot}Al_2O_3{\cdot}6.00H_2O$	**214**
$3CaO{\cdot}Al_2O_3{\cdot}8.00H_2O$	**235**
$3CaO{\cdot}Al_2O_3{\cdot}10.2H_2O$	**251**
$3CaO{\cdot}Al_2O_3{\cdot}11.6H_2O$	**261**

The values given in Table VI can be considered only as preliminary. The changes in the heat effect are rather larger than one would expect were the water adsorbed by $3CaO{\cdot}Al_2O_3{\cdot}8H_2O$, but are approximately proportional to the increase in H_2O in the material. The results can hardly be considered to give conclusive evidence as to the existence of several anisotropic hydrates of tricalcium aluminate.

The Heat of Formation of Tricalcium Aluminate.—The heat of formation of tricalcium aluminate from calcium oxide and aluminum oxide may be calculated from the heats of solution of these substances in hydrochloric acid. As no experimental value for the heat of solution of aluminum oxide in hydrochloric acid is available, this must also be calculated from other thermochemical data. Using the value 68.4 kg. cal. per mole for the heat of formation of water,[16] 127 kg. cal. per gram atom as the heat of solution of aluminum in $HCl{\cdot}200H_2O$,[3] and 190.0 kg. cal. per gram atom as the heat of combustion of aluminum,[17] we obtain 79.2 kg. cal. per mole for the heat of

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[16] **Lewis, THIS JOURNAL, 28, 1390 (1906).**

[17] **Roth and** Müller, *Z. phys. Chem.*, **144,** *257* (1929).

solution of Al_2O_3 in $HCl\cdot200H_2O$. Combining this value with 46.5 kg. cal. per mole as the heat of solution of calcium oxide2" and 198 kg. cal. per mole as the heat of solution of tricalcium aluminate in $HCl\cdot200H_2O$, one obtains 20.7 kg. cal. per mole for the heat of formation of $3CaO\cdot Al_2O_3$ from CaO and Al_2O_3 at 20°.

Summary

1. The heat of solution of tricalcium aluminate in hydrochloric acid (1 g. of $3CaO\cdot Al_2O_3$ to 19.4 g. of HCl) was found to be 736.4 $cal._{20}$ per gram of $3CaO\cdot Al_2O_3$ in $HCl\cdot20H_2O$ or 732.8 $cal._{20}$ per gram in $HCl\cdot200H_2O$ at 20°.

2. The heat of solution of the isotropic (regular) hydrate of tricalcium aluminate ($3CaO\cdot Al_2O\cdot6H_2O$) in hydrochloric acid (1 g. of anhydrous $3CaO\cdot Al_2O_3$ to 26.5 g. of HCl) was found to be 523.1 $cal._{20}$ per gram of anhydrous aluminate in $HCl.20H_2O$ or 518.8 $cal._{20}$ per gram in $HCl\cdot200H_2O$ at 20°.

3. The heat of solution of tricalcium aluminate in $HCl\cdot200H_2O$ was found to be independent of the amount of acid of this concentration used in excess of the above ratio of aluminate to acid.

4. The calculated heat of hydration of tricalcium aluminate to the hexahydrate is 214 $cal._{20}$ per gram at 20°.

5. Preliminary values were obtained for the heat of solution in $HCl\cdot20H_2O$ of samples of anisotropic (hexagonal) hydrates of tricalcium aluminate containing 8, 10.2 and 11.6 moles of water of hydration per formula weight of $3CaO\cdot Al_2O_3$.

6. The specific heat of hydrochloric acid of the concentration $HCl\cdot20H_2O$ was determined between 16 and 20° as compared with water over the same temperature interval and the value 0.8507 was obtained.

7. The value of 77 calories per gram was obtained for the calculated heat of formation of tricalcium aluminate from lime (CaO) and alumina (Al_2O_3) at 20°.

SASKATOON, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

STUDIES IN DIFFUSION. 11. A KINETIC THEORY OF DIFFUSION IN LIQUID SYSTEMS

BY J. HOWARD ARNOLD

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The experimental study of diffusion in liquid systems was begun by Graham about 1850. A few years later Fick,[1] from analogy with Fourier's law of thermal conduction, enunciated the basic law of diffusion. In 1879 Stefan[2] showed that the data of Graham harmonized with Fick's Law, and developed the theory of liquid diffusion further along the same lines as his theory of diffusion in gaseous systems.[3] The equation given

$$dN/d\Theta = DA\,dc/dx$$

by Fick rests upon the assumption that the driving force causing diffusion is proportional to the concentration gradient. The use of the equation requires the evaluation, by measurement or estimation, of the proportionality constant D, usually termed the diffusion coefficient or diffusivity.

TABLE OF NOMENCLATURE

(1) — Subscript referring to diffusing substance (solute)
(2) — Subscript referring to solvent medium
A — Area of contact; abnormality factor for compounds containing active oxygen or nitrogen
a, A', B' — Proportionality constants
B — Universal constant in the equation for D
b — Temperature coefficient
c — Concentration, in moles per cubic centimeter
D — Diffusion coefficient (diffusivity), $\text{cm.}^2/\text{sec.}$ or $\text{cm.}^2/\text{day}$
d — Differential operator
F — Factor used to allow for resistance due to intermolecular forces
M — Molecular weight
m — Weight of a single molecule
N — Number of moles of substance transferred
R — Gas constant, in $pV = RT$
r — Radius of diffusing particle
S — $V_1^{1/3} + V_2^{1/3}$; represents the sum of the molecular diameters
T — Absolute temperature, degrees Kelvin
t — Temperature, degrees centigrade
u — Net forward velocity of diffusion
V — Volume of one mole of liquid; refers to b. p. for the calculation of S
v — Specific volume
w — Molecular velocity of thermal agitation
x — Distance, measured in the direction of diffusive flow
Z — Solvent viscosity, in centipoises
Θ — Time, in seconds or days

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[1] Fick, *Ann. Phys.*, 94, *59* (1855).

[2] Stefan, *Wien. Ber.*, 79, 161 (1879)

[3] Lewis and Chang, *Am. Inst. Chem. Eng.. 21*, 135 **(1928).**

Numerous attempts to correlate the values of D obtained experimentally and the properties of the substances involved have been made during the past fifty years; none has been a pronounced success, and all have lacked generality. The principal difficulty in the way of the development of a rational theory of diffusion in liquid systems has been the absence of a kinetic theory of liquids corresponding to that of gases. Attempts at correlation have proceeded along two diametrically opposite lines, the kinetic and the hydrodynamic, as represented by the Exner Rule and the Stokes–Einstein Equation.

From kinetic theory it is known that in any gaseous system the average kinetic energy of a molecule is a function of temperature only

$$mw^2 = \text{constant}$$

It is seen from this that the translational velocity of the molecule is inversely proportional to the square root of the molecular weight; if we make the simple assumption that the rate of diffusion varies directly as the translational velocity, the diffusivity varies inversely as the square root of the molecular weight (Graham's Law). In 1875 Exner[4] applied this rule to the diffusion of gases through liquids, and showed that it is in agreement, approximately, with the experimental data. This work was continued by Hüfner,[5] who later extended it to substances other than dissolved gases, as did Euler[6] and Pickering.[7] The rule has been exploited by a number of other investigators, among them Thovert,[8] Öholm,[9] and Carlson.[10] More recently, Smith,[11] using Öholm's data, defined D/M as the "ideal diffusion coefficient," which was then shown proportional inversely to the $3/2$ power of M.

In 1858, Wiedemann[12] found that D varied inversely as the solvent viscosity, thereby laying the foundation for numerous attempts at correlation along hydrodynamical lines. This fact was combined by Walden[13] with the Exner Rule, giving the relation

$$DZM^{1/2} = \text{constant}$$

The equations of Wiedemann and Walden were tested for a large number of systems by Thovert,[14] and found to conform approximately to the observed facts.

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[4] Exner, *Ann. Phys.*, 155, 443 (1875).

[5] Hüfner, *ibid.*, 16, 253 (1882); 60, 134 (1897); Z. *physik. Chem.*. 27, 227 (1898).

[6] Euler, *Ann. Phys.*, 63, 273 (1897).

[7] Pickering, *Phil.* Mag., 35, 127 (1893)

[8] Thovert, *Compt. rend.*, 135. 579 (1902).

[9] Öholm, Z. *physik. Chem.*, **70**, 378 (1910).

[10] Carlson, THIS JOURNAL, 33, 1027 (1911).

[11] Smith, *ibid.*, 36, 847 (1914); 37, 722 (1915)

[12] Wiedemann, Ann. *Phys.*, 104, 170 (1858)

[13] Walden, Z. *Elektrochem.*, 12, 77 (1906).

[14] Thovert, *Compt. rend.*, 138, 481 (1904); Ann. *de Phys.*, 2, 369 (1914).

In 1905 Sutherland[15] and Einstein[16] independently derived what is now known as the Stokes–Einstein equation. Sutherland applied the relation

$$D = \frac{RT}{6\pi NZr}$$

(N here is Avogadro's number) to the existing data, but finding the agreement poor, discarded it in favor of the empirical equation

$$V = A'/V + B'/V^{1/3}$$

Einstein, who derived the relation in the course of his investigation of the Brownian movement of colloidal particles, indicated its possible usefulness in molecular diffusion, but did not apply it to the existing data; this has been done by von Wogau,[17] Groh and Kelp, Svedberg[18] and Miller, resulting in the conclusion that the equation is only approximately true for the diffusion of molecules, though accurate for colloidal particles. Its breakdown is due to the inapplicability of Stokes' law, which assumes the solvent to be a continuum, a postulate no longer satisfied when the diffusing particle approaches the solvent molecules in size. It also possesses the obvious fault of including only the viscosity of the solvent and the radius of the diffusing particle, which are certainly insufficient to specify the behavior of the system; similar objections apply to the Exner Rule. It may be noted that Gapon and Muchin[19] have derived an equation similar to the Stokes–Einstein, but including other variables than r and z.

Riecke[20] found a relation between the diffusivity and the mean free path of the diffusing molecule, but as he did not evaluate the free path length, the theory is incomplete. His theory is essentially the same as the usual kinetic theory of diffusion in gases. Enskog[21] has also made a preliminary attempt to apply gas theory to liquid diffusion.

In the absence of a classical kinetic theory of liquids, there has arisen in recent years a tendency to apply the kinetic theory of gases directly to liquid systems, usually with the introduction of a free space factor to take account of the fact that the close packing of the molecules must necessarily interfere with their freedom of motion. In this manner Christiansen,[22] Norrish and Smith[23] and Jowett[24] have made use of the gas theory expression for collision rate in their studies of reaction velocity

[15] Sutherland, *Phil. Mag.*, 9, 781 (1905).

[16] Einstein, *Ann. Phys.*, 17, 549 (1905).

[17] Von Wogau, *Ber. physik. Ges.*, 6, 542 (1908).

[18] Svedberg, "Existenz der Molekiile," p. 60.

[19] Gapon and Muchin, *Ukrainskii Khem. Zhur.*, 2, 459 (1926).

[20] Riecke, *Z. physik. Chem.*, 5, 564 (1890).

[21] Enskog, *Svenska Vet. Ak.*, 63, 4 (1922).

[22] Christiansen, *Z. physik. Chem.*, 113, 35 (1924).

[23] Norrish and Smith, *J. Chem. Soc.*, 129 (1928).

[24] Jowett, *Phil. Mag.*, 8, 1059 (1929).

in liquid systems. Lenard[25] follows a similar course in his consideration of ionic mobility.

It is the purpose of this paper to demonstrate that the classical kinetic theory expression for gaseous diffusivity may be applied to liquid systems, provided that due regard be taken of the complications introduced by the close packing of the molecules. We shall first apply gas theory directly to liquid diffusion, later modifying the equation so obtained to allow for the failure of several assumptions made for gases. The derivation which follows closely parallels that of Stefan[26] for gaseous diffusion.

Fick's law states that the diffusion rate is proportional to the concentration gradient

$$\mathrm{d}N_1/A\mathrm{d}\Theta = D\mathrm{d}c_1/\mathrm{d}x$$

If we represent by u_1 the net forward velocity of a molecule in the diffusion stream

$$\mathrm{d}N_1/A\mathrm{d}\Theta = c_1u_1$$

It may easily be shown by calculation that the acceleration of the diffusing molecules is negligibly small; in the absence of external forces, the driving force $\mathrm{d}c/\mathrm{d}x$ is used solely to overcome the resistance to diffusion, measured in terms of the momentum transferred from the diffusing solute to the solvent. This momentum transfer is equal to the product of the total number of collisions of unlike molecules by the momentum loss per collision. From gas theory the number of collisions per second is proportional to the concentration of each type of molecule, to an "average" molecular cross-sectional area, and to the root mean square molecular velocity; that is, to

$$c_1c_2\,S^2\sqrt{w_1^2 + w_2^2} \tag{3}$$

where S^2 represents the square of the sum of the molecular diameters. At constant temperature, all the molecules in the system have, on the average, the same kinetic energy; w^2 therefore varies inversely as the molecular weight, since Mw^2 is constant, and Expression 3 becomes

$$c_1c_2\,S^2\sqrt{\frac{1}{M_1} + \frac{1}{M_2}} \tag{4}$$

For forceless spheres, the momentum loss per collision is

$$2/3\,\frac{m_1m_2}{m_1 + m_2}\,(u_1 + u_2) \tag{5}$$

Since the mass of a single molecule, m, is proportional to the molecular weight, M, Expression 5 may be written

$$\frac{(u_1 + u_2)}{\frac{1}{M_1} + \frac{1}{M_2}} \tag{6}$$

$u_1 + u_2$ being the relative velocity of unlike molecules.

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[25] Lenard, Ann. *Physik,* 61,665 (1920).

[26] Stefan, *Wien.* Ber., 65, 323 (1872); cf. Sutherland, Phil. Mag., 38, 1 (1884).

Assuming no volume change on mixing, we may write the equation of continuity to express the constancy of volume

$$c_1V_1u_1 - c_2V_2u_2 = 0 \tag{7}$$

since the sum of the partial volumes equals the total volume

$$c_1V_1 + c_2V_2 = 1 \tag{8}$$

Combining Equations 7 and 8

$$(u_1 + u_2) = u_1\left(1 + \frac{c_1V_1}{c_2V_2}\right) \tag{9}$$

From 4, 6 and 9 the resistance to diffusion is found to be proportional to

$$\frac{c_1c_2\, S^2\, u_1}{c_2V_2\sqrt{\dfrac{1}{M_1} + \dfrac{1}{M_2}}} \tag{10}$$

From Equations 1 and 2

$$\mathrm{d}c_1/\mathrm{d}x = c_1u_1/D \tag{11}$$

On setting the driving force $\mathrm{d}c_1/\mathrm{d}x$ equal to the resistance and solving for D we have

$$D = \frac{B\sqrt{\dfrac{1}{M_1} + \dfrac{1}{M_2}}}{S^2}\,(V_2) \tag{12}$$

where B is a proportionality constant. Except for the V_2, this is identical with the expression derived by Stefan for gaseous diffusion.

In the derivation of Equation 12 three assumptions relative to the collision rate have been made, *viz.*, (1) that all collisions are binary, involving two molecules only; (2) that the collision rate is unaffected by the volume occupied by the molecules, which in a gas is negligibly small compared to the total volume; and (3) that the intermolecular attractions do not come into play. While in the kinetic theory of gases these assumptions may be allowable, in the treatment of liquid diffusion none of them can be considered valid because of the greater molecular density in the liquid state. As far as the writer is aware, no molecular analysis of the problem of collision rate in liquid systems has been made; in this paper we shall take account of the failure of the three assumptions mentioned in a semi-empirical way, by means of a factor F to be inserted in the denominator of Equation 12, this factor being evaluated by a study of the available data on liquid diffusion.

Since roughly one-third of the volume of a liquid is occupied by the molecules themselves, it is apparent that a fairly large fraction of the collisions will be of an order higher than the second, on account of the very close packing. It has been shown by Syrkin[27] that the expression for the rate of higher order collisions is of a form similar to Equation 4; as will be seen later, we may assume to a sufficient approximation that the simpler expression (4) is applicable.

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

The effect on collision rate of the volume occupied by the molecules was first evaluated for gases by van der Waals[28] in developing his equation of state. For gases, the correction factor obtained is always a function of the ratio b/V, where b is proportional to the actual volume of the molecules and V is the apparent volume. In the gaseous state, b/V is very small, while for a liquid it is roughly unity; however, in a liquid, V is no longer constant as required by Avogadro's law, but varies from liquid to liquid over a wide range. At the boiling points, or other corresponding temperatures, the actual volume of the molecules is the same fraction of V for all liquids, hence b/V becomes the same for all liquids. The correction factor therefore varies from liquid to liquid only in so far as V at the given temperature differs from V at the boiling point; because of the low coefficients of expansion of liquids, this variation will not be large. Moreover, the correction factor is probably quite insensitive to moderate variations in b/V, and, since most liquids are not far removed from their boiling points at ordinary temperatures, we may safely suppose that this factor is constant for all systems, as a working approximation; exceptions will be met with in the case of high-boiling solvents.

The third assumption, that intermolecular forces may be neglected, is not tenable even in the theory of gaseous diffusion, and much less so in the case of liquids. Presumably because of induced curvature in the molecular paths, such forces cause a very considerable increase in the collision rate; the effect is a specific one, depending on the nature of the molecules composing the system, and varying over an extremely wide range. The effect of molecular forces on gaseous viscosity and diffusion was considered by Sutherland,[29] who arrived at a dynamical solution of the problem; the application of Sutherland's equations to gaseous diffusion is treated in the first paper of this series.[30] In the present state of liquid kinetic theory, a dynamical analysis of the problem is impossible; we shall therefore evaluate the factor F in terms of other properties of the system as parameters, thereby avoiding the necessity for such an analysis. Since F is intimately connected with the total transfer of momentum within the fluid, it is logical to relate it to the viscosity of the medium, which is a measure of such transfer.

By the empirical examination of the existing data on the diffusion of non-electrolytes, several rules for the variation of F with the nature of the system have been determined. In this paper we shall be concerned only with the data for low concentrations of diffusing substance, *i. e.*, for dilute systems, a condition satisfied by practically all the existing data.

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[28] Jeans, "Dynamical Theory of Gases," pp. 125 ff.; Loeb, "Kinetic Theory of Gases," pp. 130 ff.

[29] Sutherland, *Phil. Mag.*, 36, 507 (1893); 38, 1 (1894).

[30] Arnold, *Ind. Eng. Chem.*, 22, 1091 (1930).

1. For dilute systems, F is essentially a function of the solvent properties only, being nearly independent of the nature of the diffusing substance; thus the diffusion data for a number of solutes in any given solvent obey the same law found for gaseous diffusion, except for the proportionality constant. This rule is not strictly true, some dependence of F on solute properties being noted, but the meagerness of the available accurate data prevents the more accurate determination of the nature of this dependence.

2. F is directly proportional to the square root of the solvent viscosity. For high-boiling solvents indications are that some modification of this rule is necessary; this also is hampered by scarcity of data.

3. When either solvent or solute, or both, belongs to the class of substances commonly regarded as "associated," factors A_1 and A_2 (for solute and solvent, respectively) must be inserted in the expression for F. Such substances are those containing an unsaturated oxygen or nitrogen atom, *e.* g., water, alcohols, acids, amines, etc., whose molecules as a result of this unsaturation possess unduly large attractive forces, and consequently show anomalies in many physical properties. With such substances the resistance to diffusion is found to be higher than can be accounted for by the first two rules, necessitating the use of the "abnormality factor," A.

The complete expression for F is therefore

$$F = A_1A_2V_2Z_2^{1/2} \tag{13}$$

the V_2 in this expression canceling that in Equation 12, as is found necessary for proper correlation. The final equation for D to be tested is then

$$D = \frac{B\sqrt{\frac{1}{M_1} + \frac{1}{M_2}}}{A_1A_2Z_2^{1/2}S^2} \tag{14}$$

As a standard temperature of comparison, we shall use 20°, conversions to this temperature being made with the aid of the coefficients discussed later. Z_2 is expressed in centipoises at 20°; S is the sum of the cube roots of the molecular volumes of solute and solvent, found with the aid of the Kopp–Le Bas system of calculation as described in the previous paper.

To test the first rule governing F, we require data on the diffusion of normal substances in a single solvent; these are supplied by the experiments of Thovert,[31] using benzene as the solvent. Table I contains values observed at 15°, in cm.^{2}/sec., X 10^{-5} together with D_{calcd} found with the aid of a graphically determined value of B of 0.00918 at 15°, or 0.0100 at 20°. The agreement is not exact, the ratio of calculated to observed D tending to rise with increasing molecular weight; the median deviation is 8%, which is not to be considered serious inasmuch as the probable

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[31] Thovert, *Ann. phys.*, [9] **2, 415 (1914).**

experimental error is about 5% or even more. We shall therefore assume that F is approximately independent of solute nature, for normal solutes.

TABLE I

DIFFUSION IN BENZENE (THOVERT)

Diffusing solute	V	S^2	$\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}$	$D_{\text{calcd.}}$	$D_{\text{obs.}}$
Chloroform	92.3	83.4	0.1456	2.00	2.11
Bromoform	99.5	85.0	.1295	1.74	1.62
Iodoform	129.5	92.9	.1238	1.53	1.38
Ethylene dichloride	93.6	83.2	.1514	2.08	2.45
Ethylene dibromide	98.4	84.5	.1347	1.83	1.97
Ethylene di-iodide	118.4	90.1	.1280	1.63	1.40
Trichloropropane	136.7	94.9	.1400	1.69	1.72
Ethyl ether	107.2	87.2	.1623	2.10	2.21
Methyl salicylate	161.5	100.6	.1392	1.59	1.56
Chlorobenzene	116.9	89.9	.1474	1.87	2.15
Dichlorobenzene	137.8	95.3	.1400	1.68	1.90
Bromobenzene	119.3	90.4	.1384	1.75	1.86
Dibromobenzene	142.6	96.4	.1307	1.56	1.37
Iodobenzene	129.3	92.9	.1330	1.64	1.50
Chloronaphthalene	170.1	102.6	.1383	1.54	1.20
Dichloronaphthalene	191.0	107.0	.1338	1.43	1.40
Bromonaphthalene	172.5	103.2	.1330	1.47	1.30
Dibromonaphthalene	195.8	108.0	.1277	1.35	1.25
Nitrobenzene	122.7	91.4	.1447	1.81	1.84
Dinitrobenzene	149.4	97.8	.1370	1.60	1.54
Trinitrobenzene	176.1	103.8	.1310	1.44	1.39
Chloronitrobenzene	143.6	96.6	.1430	1.70	1.70
Bromonitrobenzene	146.0	97.2	.1332	1.57	1.33
Nitronaphthalene	175.9	103.8	.1363	1.50	1.39
Dinitronaphthalene	202.6	109.4	.1320	1.38	1.23

The relation of *F* to solvent viscosity is well shown by the data of Miller[32] on the diffusion of iodine (Table II). The values for diffusion in ether and ethyl alcohol are due to Groh and Kelp,[33] whose values for benzene, carbon disulfide, and chloroform agree closely with those of Miller. The units of D are cm.^{2}/day, at 20°; converted to these units, the B found from Thovert's data is (0.01) (86400) or 864, which is found to be satisfactory for the correlation of Miller's data as well. The last column of Table II contains the ratio of calculated to observed D, assuming A_1 and A_2 of Equation 14 to be unity; for most of the solvents the ratio is seen to be nearly unity, indicating the correctness of our theory. Heptane is anomalous, for no apparent reason, while the high-boiling solvents anisole, phenetole, ethylene dibromide and acetylene tetrabromide show rather large deviations which will be mentioned further below. For

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[32] Miller, *Proc. Roy. Soc.* (London), 106, 724 (1924).

[33] Groh and Kelp, *Z. anorg.* Chem., 147, 321 (1925).

acetic acid, methanol, ethyl alcohol and water, the ratio is much larger, since these substances are abnormal and A_2 is greater than unity. As will be shown below, A_2 is a constant characteristic of the solvent, paralleling in magnitude the familiar "association factor" found from surface tension or similar anomalous properties of abnormal liquids.

TABLE II

DIFFUSION OF IODINE (MILLER)

Solvent	V	$Z^{1/2}$	$D_{\text{calcd.}}$	$D_{\text{obs.}}$	Calcd./Obs.
Benzene	96.0	0.801	1.81	1.670	1.08
Toluene	118.2	.763	1.67	1.686	0.99
m-Xylene	140.4	.802	1.41	1.454	.97
Bromobenzene	119.3	1.065	1.01	1.038	.97
Chloroform	92.3	0.761	1.83	1.831	1.00
Carbon tetrachloride	113.2	.976	1.11	1.177	0.94
Carbon disulfide	66.0	.613	2.70	2.697	1.00
Heptane	162.8	.693	1.58	2.386	0.66
Ethyl acetate	1082	.675	1.96	1.859	1.06
Amyl acetate	174.8	.934	1.04	1.071	0.97
Ether	107.2	.493	2.88	2.90	.99
Anisole	129.2	1.040	1.11	0.977	1.14
Phenetole	151.4	1.147	0.91	.843	1.08
Ethylene dibromide	98.4	1.310	.81	.719	1.13
Acetylene tetrabromide	145.0	3.127	.255	.1576	1.62
Acetic acid	63.8	1.120	1.65	.887	1.86
Ethyl alcohol	59.2	1.100	191	1.02	1.88
Methanol	37.0	0.781	3.64	1.572	2.325
Water	18.4	1 005	4.48	0.832	5.38

Table III contains the data of Öholm[34] for the diffusion of bromoform through various solvents, with the calculated values of A_2 shown in the last column. Table IV gives the data of Dummer,[35] whose work is of especial interest because of his use of several substances both as solvent and as solute. Although he used 10 and 20% solutions, the effect of

TABLE III

DIFFUSION OF BROMOFORM (OHOLM)

Solvent	V	S^2	$Z^{1/2}$	$D_{\text{calcd.}}$	$D_{\text{obs.}}$	A_2
Ethyl ether	107.2	88.0	0.493	2.64	2.98	(0.89)
Benzene	96.0	85.0	.801	1.65	1.53	(1.08)
Acetone	74.0	78.2	.570	2.83	2.37	1.19
Water	18.4	53.0	1.005	3.98	0.85	4.70
Methanol	37.0	63.6	0.781	3.27	1.71	1.91
Ethyl alcohol	59.2	73 0	1.100	1.74	0.85	2.04
Propyl alcohol	81.4	80.7	1.492	1.03	.76	1.36
Amyl alcohol	103.6	87.2	2.00	0.62	.54	1.14
(Bromoform)	99.5	..	..	..	..	

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[34] Öholm, Medd. Nobelinst., 2, 23(1913).

[35] Dummer, *Z. anorg. Chem.*, **109**, 49(1919).

concentration on D is not great, and the agreement throughout is satisfactory. For methanol, nitrobenzene and acetone, values of A_2 of 2.0, **1.35** and 1.15 are required for good correlation. All values in Tables III and IV are in cm.^{2}/day at 20°.

TABLE IV

DIFFUSION OF ORGANIC SUBSTANCES (DUMMER)

System	V	S^2	$\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}$	$D_{\text{calcd.}}$	$D_{\text{obs.}}$
In ethyl acetate: (1) (0.675)=$AZ^{1/2}$					
Nitrobenzene	117.6	93.8	0.1395	1.91	1.94
Benzo-trichloride	180.9	108.6	.1282	1.52	1.69
Ethyl benzoate	174.6	107.0	.1340	1.61	1 6 0
In ethyl benzoate: (1) (1 48)					
Nitrobenzene	117 6	110 0	0 1217	0.65	0.63
Nitromethane	51 2	86 7	.1517	1 02	.91
Benzo-trichloride	180 9	126 0	1085	.51	.41
Ethyl acetate	1082	107.0	1340	74	.77
Acetone	74 0	96 0	1544	95	91
In benzo-trichloride: (1) (1.53)					
Ethyl acetate	108.2	108.6	0.1282	0.67	0.66
Ethyl benzoate	174.6	126.0	.1085	.49	.45
In methanol: (2.0) (0.781)					
Nitromethane	51.2	49.8	0.194	2.16	2.39
Nitrobenzene	117.6	68.0	.197	1.61	1.56
Ethyl acetate	108.2	65.5	.206	1.74	1.79
Ethyl benzoate	174.6	79.7	.195	1.36	1.37
Acetone	74.0	56.9	.220	2 14	2.31
In nitrobenzene: (1.35) (1 41)					
Nitromethane	51.2	74.5	0.1562	0.95	0.83
Ethyl acetate	108.2	93.8	.1395	.68	.68
Ethyl benzoate	174.6	110.0	.1217	.50	.50
Acetone	74.0	83.0	.1590	.87	.80
In acetone: (1.15) (0.570)					
Nitrobenzene	117.6	83.0	0.1590	2.54	2.54
Ethyl benzoate	174.6	96 0	.1544	2.13	2.13

Table V contains data from Thovert[31] for the diffusion of normal solutes in methanol, in cm.^{2}/sec. X 10^{-5} at 15°. Using the abnormality factor 2.0 found from Dummer's data for methanol, satisfactory correlation is obtained, the deviations being of the same nature and magnitude as in Table I. It may be noted here that Thovert's results are somewhat erratic, with considerable errors in some instances; the general accuracy of his work is quite uncertain.

TABLE V

DIFFUSION OF NORMAL SOLUTES IN METHANOL (THOVERT)

Substance	*V*	S^2	$\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}$	D_{calcd}	$D_{\text{obs.}}$
Carbon tetrachloride	113.2	67.0	0.1940	1.70	1.69
Chloroform	92.3	62.0	1993	1 90	2.07
Ethylene di-iodide	118.4	68 0	1866	I 62	1.56
Trichloropropanc	136.7	72 2	1954	1.59	1.76
Allyl bromide	89.9	61.1	1990	1 92	2.22
Allyl iodide	99.0	Ad.9	1930	1.78	1.78
Acetonitrile	66.3	51.5	2360	2 70	2:64
Ethyl ether	107.2	65.4	,2120	1.92	2.00
Ethyl nitrate	85.9	60.0	.2060	2 02	2.18
Quinone	108.4	66.0	.2015	1.80	1.84
Methyl salicylate	161.5	77.1	1972	1.51	1.56
Nitrobenzene	122.7	69.2	.1985	1.69	1.81
Dinitrohenzene	149.4	74.8	1930	1.52	1.56
Nitronaphthalene	175.9	80.0	1925	1.42	1.50
Dinitronaphthalene	202.6	85.0	1892	1.32	1.32
Chloronaphthalenc	170.1	79.0	,1940	1.45	1.38
Dichloronaphthalene	191.0	83.0	.1905	1.35	1.52
Chlorobenzene	116.9	66.1	2005	1.79	2.07
Bromobenzcne	119.3	68.4	1940	1.67	1.79
Iodobenzene	129 4	70 5	.1903	1.59	1.65

As noted above, when the solvent is abnormal, the calculated D must be brought into agreement with the observed ***D*** by the use of the abnormality factor A_2; it is also found that abnormal ***diffusing substances*** require the introduction of a factor A_1, quite independently of the abnormal or normal nature of the solvent. This is clearly shown by Table VI, the values of ***D*** calculated on the assumption of an A_1 of unity being uniformly too high; the ratio $D_{\text{calcd.}}/D_{\text{obs}}$ is then equal to the factor A_1. The last column contains values of A_1 found similarly from Thovert's data on diffusion in methanol; in most cases these agree closely with the values for benzene solution, indicating that the abnormal diffusional behavior of the solute is not greatly influenced by the nature of the solvent (see, however, the discussion of Table X).

Table VII contains data by Öholm[34] for the diffusion of both normal and abnormal solutes in ethyl alcohol; values of D are given in cm.²/day, at 20°, extrapolated to zero concentration. To a close approximation, the A_2 for ethyl alcohol may be taken as 2.0, as for methanol. The last column gives, for the abnormal solutes, the values of A_1 calculated from Thovert's data on diffusion in methanol, as in Table VI.

We have next to consider the data for diffusion in aqueous solution. In order to arrive at an abnormality factor A_2 for water, we are limited to the consideration of normal solutes only; unfortunately, nearly all substances which are water-soluble are also abnormal. In Table III

TABLE VI

DIFFUSION OF ABNORMAL SOLUTES IN BENZENE (THOVERT)

Substance	V	S^2	$\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}$	$D_{\text{calcd.}}$	$D_{\text{obs.}}$	A_1	A_{MeOH}
Formic acid	41.3	64.6	0.1567	2.78	2.16	1.29	1.53
Acetic acid	63.7	73.6	.1716	2.66	1.92	1.38	1.53
Chloro-acetic acid	94.6	83.4	.1530	2.10	1.48	1.42	1.28
Benzoic acid	130.2	92.9	.1450	1.79	1.36	1.32	1.26
Phthalic acid	164.4	101.2	.1372	1.55	1.37	1.13	1.12
Benzaldehyde	122.8	91.6	.1490	1.86	1.73	1.07	1.03
Salicylaldehyde	130.2	93.3	.1450	1.78	1.78	1.00	0.94
Quinone	108.4	87.6	.1485	1.94	1.68	1.15	.98
Propyl alcohol	103.6	86.3	.1720	2.28	1.60	1.42	..
Amyl alcohol	125.8	92.0	.1522	1.91	1.48	1.29	1.29
Phenol	103.4	86.1	.1530	2.04	1.54	1.32	1.35
Chlorophenol	124.3	91.8	.1437	1.79	1.42	1.26	1.26
Bromophenol	126.7	92.3	.1363	1.69	1.34	1.26	1.21
Chloro-aniline	131.1	93.5	.1440	1.76	1.56	1.13	1.18
Bromoaniline	133.5	93.9	.1363	1.66	1.41	1.18	1.15

TABLE VII

DIFFUSION IN ETHYL ALCOHOL (ÖHOLM)

Substance	V	S^2	$\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}$	$D_{\text{calcd.}}$	$D_{\text{obs.}}$	A	A_{MeOH}
Iodobenzene	129.3	80.6	0.163	0.79	0.85	(0.93)	..
Bromonaphthalene	172.5	90.0	.163	.71	.68	(1.04)	..
Chloroform	92.3	71.2	1.73	.95	1.07	(0.89)	..
Bromoform	99.5	73.0	.160	.86	0.85	(1.01)	..
Azobenzene	205.6	96.2	.165	.67	.65	(1.03)	..
Stearic acid	419	129.3	.159	.48	.50	(0.96)	..
Acetal	162.6	88.0	.174	.78	.98	(.80)	..
Camphor	214.5	97.6	.168	.67	.62	1.08	..
Pyridine	93.1	71.2	.185	1.02	.95	1.07	1.26
Allyl alcohol	74.0	65.7	.197	1.18	.83	1.42	1.27
Amyl alcohol	125.8	79.0	1.79	0.89	.68	1.31	1.29
Chloral	114.5	76.8	.169	.86	.56	1.53	1.40
Saligenin	133.0	81.0	.172	.83	.53	1.57	..
Acetamide	71.1	65.0	.197	1.19	.57	2.08	1.54
Acetin	144	83.7	.171	0.80	.48	1.67	..
Glycerin	99.5	73.0	.181	.97	.45	2.15	1.65
Hydroquinone	110.8	76.0	.175	.90	.42	2.14	1.43
Resorcinol	110.8	76.0	.175	.90	.38	2.36	..
Cetyl alcohol	370	122.5	.160	.51	.30	1.70	..
Ethyl alcohol	59.2	..	..	..	..	2.00	..

an A_2 of 4.70 was found, which on further trial proves to be correct, giving excellent agreement with the experimental results for the diffusion of the fixed gases (Table VIII). The molecular volumes used in this table have been taken from the previous paper on gaseous diffusion, and were calculated from gaseous viscosity data; Kopp's law is rather difficultly applicable to substances of low molecular complexity. The values of $D_{\text{obs.}}$ are taken as the most reliable of those cited in Table VIII-A, which was compiled from data given by Tammann[36] in his recent review of the subject, together with values for oxygen and carbon dioxide given by

TABLE VIIX

DIFFUSION OF GASES IN WATER

Gas	V	S^2	$\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}$	$D_{\text{calcd.}}$	$D_{\text{obs.}}$
Hydrogen	14.3	25.7	0.745	5.34	5.13 (av.)
Oxygen	25.6	31.2	.294	1.73	1.80
Nitrogen	31.2	33.5	.302	1.66	1.64
Carbon dioxide	34.0	34.5	.280	1.50	1.50
Nitrous oxide	36.4	35.5	.280	1.45	1.51
Acetylene	(37.0)	35.8	.307	1.58	1.56
Ammonia	25.8	31.4	.338	1.98	1.76
Hydrogen sulfide	(33.0)	34.2	.291	1.57	1.41
Chlorine	(49.2)	39.6	.264	1.23	1.22
Water	18.4	..	...	..	

TABLE VIIIA

DIFFUSION OF GASES IN WATER (AFTER TAMMANN)

	Hydrogen				Carbon Dioxide		
	D_t	t	D_{20}		D_t	t	D_{20}
Hagenbach	2.95	14	3.48	Hagenbach	0.770	0	1.23
Exner	5.81	13	7.04	Hagenbach	.843	15	0.97
Tammann	2.95	17.5	3.17	Stefan	1.38	17	1.50
Hüfner	4.09	16	4 58	Tammann	1.25	17.5	1.34
Hüfner	4.45	21	4.32	Hüfner	1.383	15.2	1.60
Hüfner	7.53	16	8.44	Hüfner	1.264	10.3	1.63
	Ammonia			Hüfner	1.542	20.4	1.52
				Carlson	1.378	16	1.50
Scheffer	1.06	4.5	1.55				
Arrhenius	1.42	12	1.76		Oxygen		
Hüfner	1.106	15	1.27	Hüfner	1.62	21.7	1.54
Abegg	1.575	16	1.76	Tammann	2.05	17.5	2.20
Hagenbach	1.594	17	1.74	Exner	1.91	15	2.20
Exner	1.93	17	2.10	Carlson	1.607	16	1.80
Voigtländer	1.26	20	1.26		Nitrogen		
	Hydrogen sulfide			Hüfner	1.73	21.7	1.64
Hüfner	1.24	15.5	1.41	Exner	1.68	15	1.93
Hagenbach	1.53	16	1.71	Tammann	1.56	25	1.36
	Chlorine				Nitrous oxide		
Hüfner	1.10	16.3	1.22	Hüfner	1.35	16.2	1.51
Euler	1.22	12	1.51	Hagenbach	0.634	14	0.748
	Acetylene						
Tammann	1.45	17.5	1.56				

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[36] Tammann, *Z. anorg. Chem.*, 179, 125 (1929).

Carlson,[37] all data being reduced to 20° with the aid of a temperature coefficient of 0.030, and expressed in $cm.^2$/day. Especially in the case of hydrogen, disagreements among the various experimenters are apparent, and are traceable to the difficult technique involved and the low solubility of most of the gases.

Representative of the diffusion of abnormal solutes in aqueous solution, Table IX contains the data of Thovert. The dependence of A on the functional groups in the molecule is clearly shown; the aliphatic alcohols show nearly the same value of A throughout, as do formic and acetic acids. In the multiple-functioned compounds such as tartaric acid, glycerin and the sugars, internal neutralization of the abnormal forces operates to give a lower A than would be expected. When such neutralization becomes complete, an A of unity is to be expected; this is the case for

TABLE IX

DIFFUSION OF ABNORMAL SOLUTES IN WATER (THOVERT)

Substance	V	S^2	$\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}$	$D_{\text{calcd.}}$	$D_{\text{obs.}}$	A_1
Formic acid	41.3	372	0278	1.37	1.04	1.32
Acetic acid	63 7	44.0	269	1.12	0.88	1.27
Tartaric acid	135	60.3	.249	0 76	0.61	1.24
Methyl alcohol	370	35.6	295	1 52	1.28	1.19
Ethyl alcohol	59.2	42.6	278	1.24	1.00	1.24
Propyl alcohol	81.4	48.7	269	1.01	087	1.16
Butyl alcohol	103.6	53.8	.263	0.90	.77	1.16
Amyl alcohol	125.8	58.5	.259	.81	69	1.16
Allyl alcohol	74.0	46.7	270	1.06	90	1.17
Glycerin	96.2	52.2	258	0.91	.72	1.25
Chlorohydrin	109.7	55.2	254	84	76	1.11
Dichlorohydrin	1232	580	.252	80	75	1.06
Chloral hydrate	129.3	59.0	248	77	58	1.33
Phenol	103.4	53.8	257	.88	.72	1.21
Hydroquinone	110.8	55.3	254	84	.66	1.27
Pyrogallol	118.2	57.0	252	81	.56	1.45
Glucose	178	68.3	247	66	52	1.27
Mannite	185	69.4	.247	65	.50	1.30
Lactose	340	92 7	.246	49	38	1.28
Raffinose	503	112	240	39	33	1.19
Aniline	110.2	552	257	85	69	1.23
Aniline hydrochloride	138.5	61.0	.252	76	79	0.96
Urethan	103.8	53.8	.258	88	80	1.10
Urea	58.0	42.5	.269	1.16	94	1.23
Acetamide	66.0	44.6	.269	1.10	.96	1.15
Acetonitrile	56.3	42.0	.283	1.23	1.26	0.98
Pyridine	93.1	51.5	.261	0.93	0.58	1.60
Antipyrine	230.8	77.0	.247	.59	.54	1.09
Trinitrobenzene	176.1	68 0	.245	.66	69	0.96

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[37] Carlson, *Medd.* Nobelinst., 2, 2 (1913).

aniline hydrochloride, trinitrobenzene and acetonitrile. A similar effect is noted with phthalic acid and salicylic aldehyde (Table VI).

Because of the cumulative errors in experiment and theory, accurate generalizations concerning the abnormality factor A are difficult to formulate. For a given substance, A_2 is greater than A_1; that is, the abnormality is more pronounced when the substance is the solvent than when it is the solute. Thus, methyl and ethyl alcohols have an A_2 of 2.0, and an A_1 in aqueous solution of only 1.2; acetone and nitrobenzene show an A_2 of 1.15 and 1.35, respectively, but as diffusing substances are apparently nearly normal. The magnitude of A_1 is dependent to some extent on the solvent, as shown in Table X; it is seen that the tendency is for A_1 to increase as the A_2 for the solvent decreases, A_1 being generally smallest in aqueous solution. Pyridinc, however, shows the opposite tendency. The usual behavior is in accord with the Nernst–Thomson rule,[38] which is based on the diminution of molecular forces when the molecule is surrounded by a medium of high dielectric constant; as commonly expressed, good ionizing media, such as water, have high dielectric constants, while solvents with low constants favor association. Thus, intermolecular attractions will be weak, and A_1 consequently low, when the solvent dielectric constant is high.

TABLE X

SOLUTE ABNORMALITY FACTORS (A_1)

Solute	Water	Methanol	Ethyl alcohol	Benzene
Phenol	1.21	1.35	..	1.32
Amyl alcohol	1.16	1 29	1.31	1.29
Hydroquinone	1.27	1.43	2.14	..
Chloral	1.33	1.40	1.53	..
Glycerin	1.25	1.65	2.15	..
Formic acid	1.32	1.53	..	1.29
Acetic acid	1.27	1.53	..	1.38
Acetamide	1.15	1.54	2.08	..
Pyridine	1.60	1 26	1.07	..

It is to be emphasized that much better correlation is obtainable by the use of the factors A_1 and A_2 than by the use of an "association factor" as a multiplier for M and V in Equation 12, as would be required by the usual concept of the association of abnormal substances. For example, to fit the value of 1.22 for Cl_2 in Table VIII, an association factor for water of 12.6 would be required—far higher than any such factor found heretofore by other methods; using this factor for bromoform (Table III) gives a $D_{\text{calcd.}}$ of 0.68, with 0.85 observed, while for H_2 (Table VIII) the calculated value is 8.33, the observed average 5.13, and the value using our A factor, 5.34. Thus, granting the fundamental soundness of the present method of correlation, it appears that the hypothesis of molecular asso-

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[38] Turner, "Molecular Association," Longmans, Green and Co., 1915, p. 42.

ciation is insufficient to explain the data. In this connection, it is noteworthy that Longinescu[39] has apparently abandoned the concept of an actual physical combination of molecules, replacing it by the idea of an abnormally high "molecular concentration" in abnormal liquids. In the opinion of the present writer, all the anomalous properties of abnormal substances are fully as readily explainable by the concept of an abnormally strong force field around the molecule as by the assumption of association.

It is noteworthy that evidence of such association is usually very indirect, and that the several available methods for the quantitative estimation of degree of association give widely differing values of this quantity. It is hardly to be expected that such relationships as, for instance, the familiar Eötvös–Ramsay–Shields equation, will give a true value of molecular weight when the surface tension and critical temperature used in the equation are themselves abnormally high because of excessive intermolecular attraction; attempts to balance the equation by assuming an abnormal molecular weight can be productive of nothing more than empirical correlations, since a new, non-existent abnormality is assumed to compensate for the two existing ones. Similar criticisms may be applied to the related hypothesis of solvation. Inspection of Table II shows the absence of complications due to solvation, which is often assumed to be the cause of the diverse colors of iodine solutions. For instance, Hildebrand[40] has even determined equilibrium constants of solvation reactions from colorimetric data. It is evident that any actual attachment of solvent molecules to the diffusing iodine molecules would be shown by the failure of the diffusion equation to apply when the normal molecular weights and volumes are used.

The variation of diffusivity with temperature has never received a thorough investigation over a wide range. It is usual to assume D a linear function of t, according to the Nernst equation

$$D = D_0(1 + bt) \tag{15}$$

where b is the usual temperature coefficient. This relation is sufficiently accurate over short ranges, but for wide variation in temperature D is not linear in t. The Stokes–Einstein equation provides the relation

$$D \propto T/Z \tag{16}$$

Cohen and Bruins,[41] investigating the diffusion of acetylene tetrabromide in acetylene tetrachloride, found the relation to be true over the range 0–50°; Scheffer,[42] for mannitol diffusing in water, verified it from 0 to 70°.

Taking the logarithm of both sides of the last equation and differentiating gives

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[39] Longinescu, *Chem. Reviews*, **6**, 381 (1929).

[40] Hildebrand, This Journal, **42**, 2180 (1920).

[41] Cohen and Bruins, *Z. physik. Chem.*, **103**, 404 (1923).

[42] Scheffer, *V. Kon. Ak. Wet. Amst.*, **19**, 148 (1916).

$$\frac{1}{D}\frac{dD}{dT} = \frac{1}{T} - \frac{1}{Z}\frac{dZ}{dT} \qquad (17)$$

whence, by definition

$$b = 1/T - b_z \qquad (18)$$

where b_z is the corresponding temperature coefficient of viscosity. Also if instead of using the Stokes–Einstein equation, we choose to express the variation of D solely in terms of the change in Z, let

$$D = aZ^n \qquad (19)$$

from which

$$b = -nb_z \qquad (20)$$

To test these relations, we may use the data of Miller, over the range 10–20°. In Table XI the first column shows values of b_z calculated from the solvent viscosities. The second column gives values of b found from the Stokes–Einstein, relation, Equation 18, taking T to correspond to 15°, while the third column gives values of b from Equation 20, taking n as $3/2$. The fourth column contains values of b given by the empirical equation

$$b = 0.020(Zv^{2/3})^{1/2} \qquad (21)$$

Z and v both being at 20°. A study of this table indicates that the relation last given is the most satisfactory, and the Stokes–Einstein the least, though all agree fairly well with the observed values.

TABLE XI

TEMPERATURE COEFFICIENTS (MILLER)

Solvent	$-b_z$	Eq. 18	Eq. 20	Eq. 21	$b_{obs.}$
Benzene	0.0139	0.018	0.021	0.017	0.018
Toluene	.0113	.015	.017	.016	.016
Xylene	.0113	.015	.017	.017	.017
Anisole	.0147	.018	.022	.021	.024
Phenetole	.0154	.019	.023	.023	.023
Bromobenzene	.0119	.016	.018	.019	.017
Ethylene dibromide	.0144	.018	.022	.020	.020
Acetylene tetrabromide	.0333	.037	.050	.043	.041
Chloroform	.0084	.012	.013	.013	.013
Carbon tetrachloride	.0138	.018	.021	.017	.019
Carbon disulfide	.0071	.011	.011	.011	.012
Heptane	.0108	.015	.016	.016	.016
Ethyl acetate	.0104	.014	.016	.014	.014
Amyl acetate	.0140	.018	.021	.020	.021
Methanol	.0128	.017	.019	.017	.018

A study of the temperature coefficients found by Öholm[43] for diffusion in aqueous solution indicates that, like the factor F, b is (for dilute solutions) a function of the solvent properties only, converging to a value of **0.030** as solute concentration approaches zero. For concentrated solutions, b becomes greater or less than **0.030**, depending on the nature of the

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[43] Öholm, *Z. physik. Chem.*, 70, 378 (1910); *Medd. Nobelinst.*, 2, 23, 24 (1913).

Z–c curve. For dilute solutions, since b is independent of solute nature, the relations deduced from Miller's data may be used for any diffusing substance.

It is apparent from an inspection of the tables given that the theory here presented is still incomplete, and can make no claim to mathematical exactness; nevertheless, the agreement with experiment is considerably better than any hitherto attained, and indicates that the method of approach is fundamentally sound and practicable. We have now to consider the several causes to which the deviations noted may be attributed.

Experimental errors in diffusion measurements are considerable, of the order of 5% for ordinary work, and undoubtedly are responsible for much of the disagreement. The use of a Kopp law V as representing the cube of the molecular diameter is open to some criticism; it has, however, been shown in the previous paper of this series that this volume corresponds closely with that calculated from gas viscosity, and is therefore probably satisfactory for diffusion calculations. The importance of errors in V is lessened by the fact that it appears in the equation for D as a cube root. The selection of 20° as a standard reference temperature is quite arbitrary, but in the absence of a more definite knowledge of the variation of D with T, it seems advisable to choose a constant temperature near that used experimentally. The further development of the present theory will undoubtedly require the expression of F as a function of T; it is to be noted that Equation 14 is correct only at 20°, and does not completely express the variation of D with T. The factor F is analogous to the $(1 + C/T)$ of the Sutherland theory of gaseous diffusion, both representing the effect of intermolecular forces on diffusional resistance.

The greater part of the observed discrepancy is probably traceable to three causes: (1) the assumption of binary, elastic collisions in a liquid system is inexact; (2) the van der Waals correction factor is not, as assumed, constant for all systems; (3) the functional relation between F and Z is not accurately given over a wide range by Equation 13. Of these, (1) and (2) are not remediable except by further analysis of the problem, while (3) awaits further data on diffusion in viscous, high-boiling solvents. Further, neglect of the dependence of F on the solute nature introduces some error, comparable in magnitude with the experimental errors and hence not yet subject to exact evaluation. It is also to be mentioned that F may be a function of molecular volume as well as molecular force, allowing for the mean free path shortening due to the space occupied by the molecules as well as that due to intermolecular attractions. Macleod[44] has shown that liquid viscosity is very simply related to the free space within the liquid, while Equation 13 is seen to contain the solvent molecular volume as a variable affecting F. The more exact

[44] *Macleod. Trans. Faraday Soc., 19,* 6 (1923); 21, 151 (1925).

evaluation of this factor, together with the applications of the principles above discussed, to the closely related problems of diffusion in mixed solvents, ionic mobility and the diffusion of electrolytes, will be considered in a later paper.

The writer is indebted to Mr. James J. Hogan for his careful reading of the manuscript and his many helpful suggestions; to Professor Warren K. Lewis for his continued interest in the work; and to the host of experimental investigators in this field during the past eighty years, whose contributions of painstaking and accurate work have made possible the present correlation.

Summary

The classical kinetic theory of gases has been applied to diffusion in liquid systems, assuming that the resistance to diffusion is due wholly to binary collisions, and that the mean free path shortening due to the volume occupied by the molecules is the same for all systems. Allowance is made for the retarding effect of intermolecular forces by introducing a factor F, which has been found empirically to be essentially independent of the nature of the diffusing substance and directly proportional to the square root of the solvent viscosity. "Associated" substances are found to require the use of abnormality factors in the expression for F; it is found that the usual hypothesis of molecular association is incapable of explaining the diffusional behavior of these substances, and that the related hypothesis of solvation of certain substances is unnecessary for good agreement with theory. The variation of diffusivity with temperature is discussed, and several rules are given for the prediction of temperature coefficients. Comparison of the observed diffusion coefficients with those calculated from the theory shows good agreement over a wide range of molecular weights and viscosities; the sources of the deviations observed are discussed.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 265]

THE HIGH TEMPERATURE EQUILIBRIUM OF TITANIUM DIOXIDE AND CARBON WITH TITANIUM CARBIDE AND CARBON MONOXIDE

BY L. REED BRANTLEY AND ARNOLD O. BECKMAN

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Introduction

This investigation is a continuation of the researches on high temperature equilibria which have been carried out in this Laboratory.[1] The high pressure apparatus previously used in studying the equilibria between zirconium oxide and carbon,[1a] thorium oxide and carbon,[1c] and aluminum oxide and carbon[1d] was employed. The method consists in electrically heating a small graphite tube furnace which contains the solid reaction mixture, determining the temperature by an optical pyrometer, and measuring the gas pressure on a mercury manometer. The measurements described in this article include the pressures of carbon monoxide in equilibrium with the solid phases TiO_2, TiC and C over the pressure range 0.8 to 2.0 atmospheres and the temperature range 1000 to 1150°. The composition of the solid reaction mixture was determined by x-ray powder photographs.

The authors wish to express their thanks to Dr. W. B. Hincke for his suggestions and interest in this work and to Mr. F. J. Ewing for his assistance in obtaining the x-ray photographs.

Apparatus and Procedure

The apparatus was substantially the same as that used in the previous high pressure investigations.[1a,c,d] A more convenient furnace assembly was used, however, which had been developed by Dr. Hincke and one of us during the course of the investigation (unpublished) of the calcium oxide–carbon equilibrium. As is shown in Fig. 1A the graphite furnace A was supported by tungsten leads which were, in turn, connected through flexible copper cable to the water-cooled copper tubes B and C which were held rigidly co-linear by attachment to the heavy rod D. Electrode B was held in place by a micarta insulating support E; electrode C was held by a similar brass support F fitted with a thumbscrew H. The pyrex furnace bulb was sealed to the electrodes at G with sealing wax. A side tube with an inverted cup connection, also sealed with sealing wax, connected the furnace bulb with the manometer and auxiliary gas apparatus. Since the entire furnace was immersed in a water thermostat, it was necessary to protect the exposed sealing wax with paraffin.

To insert a furnace tube, the glass bulb was slipped over the lowered electrode C, which was then raised to allow the insertion of the furnace tube, after which thumbscrew H was tightened and the glass furnace bulb raised and sealed in position. It was found

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[1] (a) Prescott, THIS JOURNAL, 48, 2534 (1926); (b) 50, 3327 (1928); (c) Prescott and Hincke, *ibid.*, 49, 2744; (d) 2753 (1927); (e) 50, 3228 (1928); (f) Phys. *Rev.*, **31**, 130 (1928); *(g)* Hincke and Brantley, THIS JOURNAL, 52, 48 (1930).

that the sealing wax seals were gas tight even at two atmospheres' pressure and a furnace temperature of 2000°K.

The furnace tubes, Fig. 1B, were turned from Acheson graphite with a groove near each end to provide a central region of nearly uniform temperature within which the charge was held by graphite plugs. Two types of charge were used, one consisting of TiC and the other consisting of stoichiometric quantities of TiO_2 and graphite. In each case the materials were ground to pass through a 200-mesh sieve. The TiC was prepared by heating in *vacuo* an equimolal mixture of powdered titanium and graphite to a temperature (1950°K.) sufficiently high to volatilize any uncombined titanium metal. The TiO_2 and the metal were Eimer and Amend C. P. preparations.

When the charge consisted of TiC, the furnace was baked out in *vacuo* at a high temperature, after which the temperature was lowered to 1275 to 1350°K., and the heating continued for six to seven hours with carbon monoxide present at a pressure of about two atmospheres. When the charge consisted of TiO_2 and graphite, the furnace was heated in *vacuo* at a dull red heat for a few seconds. The apparatus was then filled with carbon monoxide at a pressure of about two atmospheres and the furnace heated to about 1750°K. for half an hour to drive off adsorbed oxygen. The furnace was then evacuated and refilled with fresh carbon monoxide at the desired pressure for the equilibrium measurements. It was found that under these conditions reaction mixtures were produced which gave satisfactory rates of reaction for the equilibrium measurements.

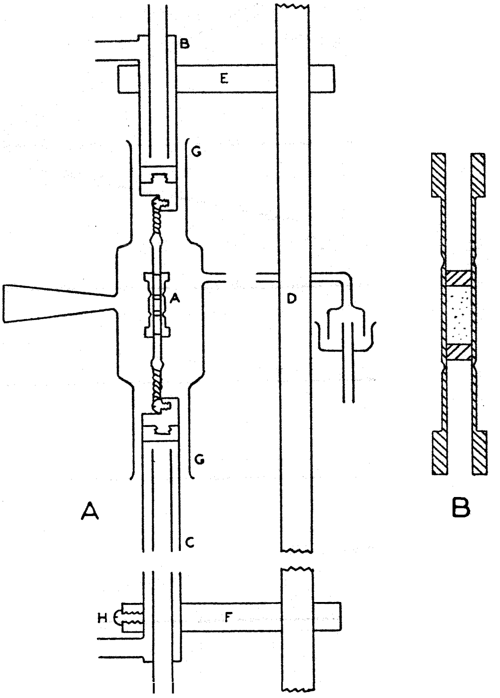
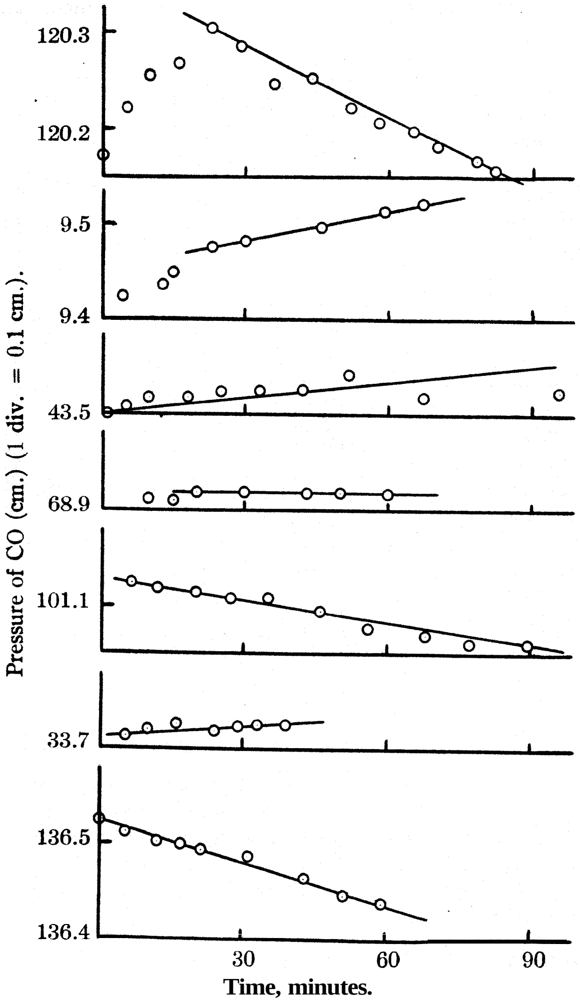


Fig. 1.—Furnace bulb and graphite furnace.

For preliminary work the furnace was heated by an alternating current from a low-voltage one-kilowatt transformer, but for the final measurements a direct current from storage batteries was used. To maintain a temperature of 1330°K. a current of about 70 amperes at 6 volts was required.

The Equilibrium Measurements

The equilibrium pressures were determined by measuring the rate of reaction (*i.* e., the rate of change of carbon monoxide pressure) at constant temperature for different pressures of carbon monoxide. By obtaining a series of both forward and reverse rates with the same furnace charge, the equilibrium pressure was found graphically as the pressure corresponding to zero rate. Typical graphs are shown in Figs. 2 and 3. In Fig. 2 are shown the carbon monoxide pressures plotted as ordinates against the time as abscissas for six successive runs at the temperature 1278°K. with different initial carbon monoxide pressures. For each run the average rate of pressure change was determined, rejecting values which were obtained during the first thirty to forty minutes of the run when the system was attaining equilibrium. These six rates are shown as ordinates in Fig. 3 with the average pressure during the run as abscissas. The intersection with the zero rate ordinate of the best straight line through these points shows the equilibrium pressure to be 60.5 cm. at this temperature.



Run	Pressure, cm.	Reaction rate (cm. X 10^3/min.)
A	120.2	−2.360
B	9.5	+1.080
C	43.5	+0.424
D	68.9	0.000
E	101.1	−0.737
F	33.7	+0.385
G	136.5	−1.473

Fig. 2.—Change of pressure with time during a typical experiment (1278°K.).

Six sets of runs of this kind were made over the temperature range 1278 to 1428°K. and pressure range from a few centimeters to two atmospheres. In some cases the initial furnace charge consisted of TiO_2 and C, and in other cases of TiC. The equilibrium pressures and corresponding temperatures are given in Table I, where Θ is the observed temperature and T is the true temperature after corrections have been made for the transmission of the window and the emissivity of carbon as in the previous work.

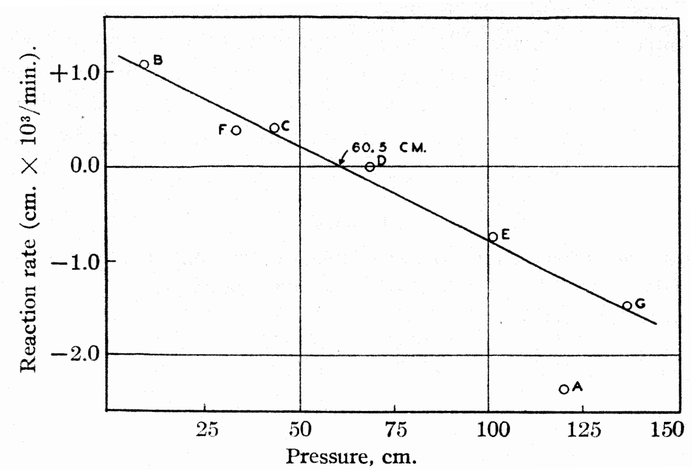


Fig. 3.—Change of reaction rate with pressure for a typical experiment (1278°K.); equilibrium pressure = 60.5 cm.

In Fig. 4 the logarithms of the equilibrium pressures are shown plotted against the reciprocals of the absolute temperatures, and it will be seen that all of the points fall upon a straight line within the experimental error.

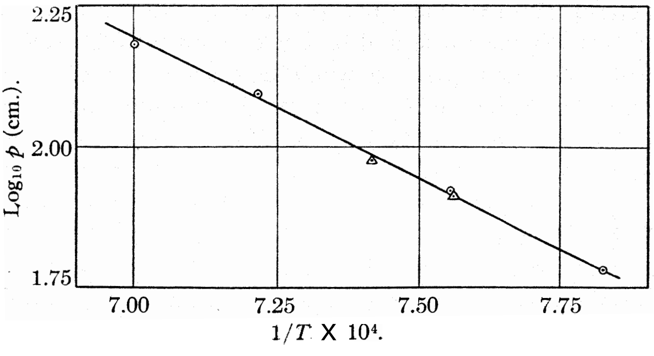


Fig. 4.—Relation between absolute temperature and equilibrium pressure of CO; circles, furnace charge initially consisted of TiO_2 + C; triangles, furnace charge initially consisted of TiC.

The relation between the equilibrium pressures and absolute temperature is given by the equation

$$\log_{10} p_{\text{atm.}} = 3.829 - 5024/T$$

A furnace charge was never used for more than two, and usually for only one, equilibrium pressure determinations. One run was attempted at 1246°K., but the reaction rates were too slow to measure accurately.

The dissociation of carbon monoxide into carbon dioxide and carbon is appreciable in this temperature range, being approximately 0.6% at 1278°K. and 0.1% at 1428°K. It is well known, however, that equilibrium is attained only very slowly. In blank experiments, using an entirely empty graphite furnace at temperatures, with carbon monoxide pressures, and over time intervals similar to those used in the equilibrium measurements, no measurable rates were observed, showing that the carbon monoxide dissociation could be entirely neglected.

TABLE I

EQUILIBRIUM PRESSURES AND FREE ENERGIES AT VARIOUS TEMPERATURES

Θ, °K	T, °K.	$1/T \times 10^4$	p (atm.)	$\text{Log}_{10} p$ (atm.)	ΔF (cal.)
1250	1278	7.825	0.796	−0.0991	+1158
1293	1323	7.559	1.081	+0.0338	− 409
1294	1324	7.553	1.114	.0469	− 568
1318	1349	7.413	1.216	.0849	−1047
1355	1386	7.215	1.634	.2133	−2703
1393	1428	7.003	1.995	.2999	−3916

The Nature of the Solid Phases

To determine the nature of the solid phases an analytical method was attempted, but the small quantities of materials available and the lack of information regarding the chemistry of the lower oxides of titanium led to the abandonment of this method. X-Ray powder photographs were finally taken of the reaction mixtures and of the various substances, namely, TiO_2 (both the rutile and brookite modifications), TiC, graphite, Ti metal and TiO, whose presence would be suspected in the reaction mixtures. The TiO was prepared by heating in the graphite furnace to 1775°K. for half an hour *in vacuo* a mixture of finely ground TiO_2 and Ti in approximately stoichiometric proportions. The work of Billy[2] has shown that TiO is formed under these conditions, although perhaps there may be some uncombined TiO_2 or Ti as well. The diameters of the rings (*i.e.*, the distances between corresponding lines on either side of the position of zero deflection) obtained on the eight photographs are represented in Fig. 5. Photographs were taken of two reaction mixtures, one (Fig. 5a) in which the initial charge was TiO_2 and graphite, and one (Fig. 5b) in which the initial charge was TiC.

The results of this investigation showed that the solid phases in the reaction mixture were TiO_2 (rutile modification), TiC and graphite. Metallic titanium, the brookite modification of TiO_2, and the lower oxide TiO were definitely shown to be absent.

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[2] Billy, Ann. *Chim.*, 16, 23 (1921).

Thermodynamic Calculations

From the results of the x-ray investigation the equilibrium studied is undoubtedly that expressed by the equation

$$TiO_2 + 3C = TiC + 2CO$$

The value of ΔF, the free energy increase attending this reaction, may be derived from the thermodynamic equation $\Delta F = -RT \ln K$, where $K = p^2$. The values of ΔF corresponding to the equilibrium pressures at various temperatures are given in the last column of Table I.

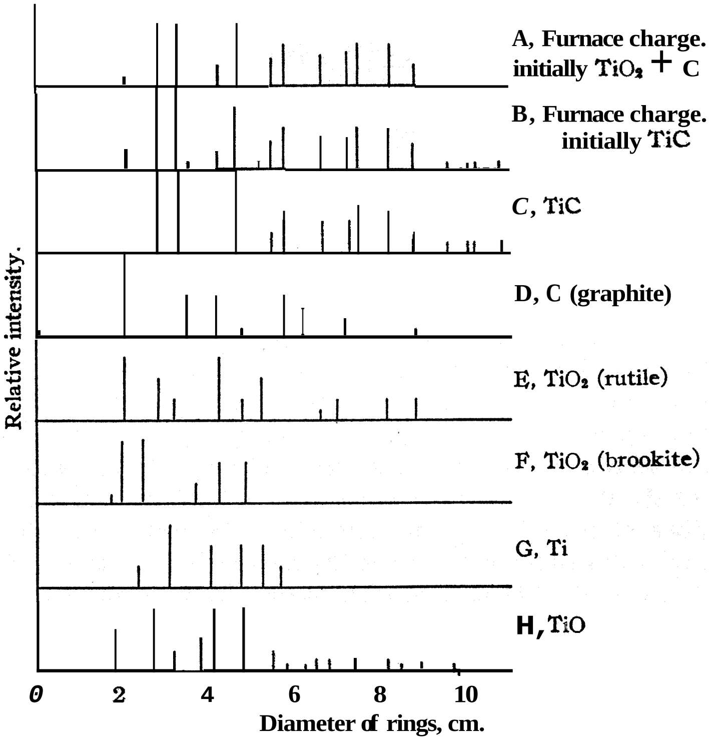

Fig. 5.—Results of x-ray powder photographs.

From the expression for $\log_{10} p$ given in the previous section, the relation

$$\Delta F = 45{,}930 - 35.01T$$

may be obtained for the temperature range 1278 to 1428°K. From this it follows that the increase in heat content, ΔH, is 45,930 calories. At 1312°K. the free energy is zero and the equilibrium pressure is one atmosphere.

Summary

Determinations have been made of the equilibrium pressures of carbon monoxide for the reaction

$$TiO_2 + 3C = TiC + 2CO$$

in the temperature range 1278 to 1428°K. The solid phases were identified by x-ray powder photographs.

Within this temperature range the increases in free energy and heat content that attend this reaction at one atmosphere pressure were found to be given by the expression A F = 45,930 − 35.01 T calories and A H = 45,930 calories. The equilibrium pressure is one atmosphere at 1312°K.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 6]

THE EFFECT OF ADDED SALTS UPON THE SOLUBILITY OF OTHER SALTS IN ETHYL ALCOHOL

BY RALPH P. SEWARD WITH WALTER C. SCHUMB

RECEIVED AUGUST 19, 1930 PUBLISHED OCTOBER 6, 1930

Introduction

The measurement of the relative solubility of a salt in a pure solvent and in the presence of other salts gives a ready measure of the change of potential or of the activity coefficient of the saturating salt These changes should be quantitatively accounted for by any adequate theory of solutions. The inter-ionic theory of Debye and Hückel[1] has achieved considerable success in describing the properties of strong electrolytes, particularly in aqueous solutions. As the inter-ionic forces vary inversely with the dielectric constant of the solvent, we may expect a more sensitive test of the theory in the case of solvents of lower dielectric constant. The number of investigations in non-aqueous solutions by which the theory may be tested is small. Solubility measurements have been made in methyl alcohol by Williams,[2] in ethyl alcohol by King and Partington,[3] in acetone by Robinson[4] and by Kraus and Seward,[5] in isopropyl alcohol by Kraus and Seward,[5] and in ethyl alcohol–water mixtures by Hansen and Williams.[6] These measurements indicate that marked deviations from the original Debye–Hückel approximation are found in aqueous and methyl alcohol solutions only in the case of higher valence salts. La Mer and Mason[7] have discussed these deviations. In solvents of lower dielectric constant, however, marked deviations have been observed in the case of univalent salts even in the most dilute solutions.

The present investigation consists of the determination of the solubility

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[1] Debye and Hiickel. *Physik. Z.*, 24, 185 (1923).

[2] Williams, THIS JOURNAL, 51, 1112 (1929).

[3] King and Partington, *Trans. Faraday Soc.*, 23, 622 (1927).

[4] Robinson, J. *Phys. Chem.*, 32, 1089 (1928).

[5] Kraus and Seward, *ibid.*, 32, 1294 (1928).

[6] Hansen and Williams, THIS JOURNAL, 52, 2759 (1930).

[7] La Mer and Mason, *ibid.*, 49, 410 (1927).

of potassium chloride in ethyl alcohol in the presence of ammonium nitrate; the solubility of potassium perchlorate in ethyl alcohol in the presence of ammonium nitrate, ammonium perchlorate and ammonium iodide; the solubility of barium nitrate in ethyl alcohol in the presence of ammonium bromide; and the comparison of the results with those predicted by the inter-ionic attraction theory.

As the inter-ionic relations should be most simple in dilute solutions, it is of importance to select salts, the saturated solutions of which are the most dilute in which their solubility may be determined with a reasonable degree of accuracy. The selection of the salts used as saturating salts was therefore determined by this consideration and that of their analytical determination. For the added or solvent salt one which was considerably more soluble and did not interfere with the analysis was selected

Preparation of Materials.—Part of the solvent used was 92% ethyl alcohol dehydrated with lime by the method recommended by W. A. Noyes;[8] part was a commercial anhydrous alcohol which was given one treatment with lime and subsequent distillation. Both samples had a density of 0.7852 at 25°.

The salts used were the purest available, further purified by recrystallization and carefully dried.

Determination of Solubilities.—The method was that used by Kraus and Seward.[6] A quantity of solvent containing a known amount of the added salt was agitated with an excess of the saturating salt until equilibrium was reached and the concentration of the saturating salt in the resulting solution determined analytically. About five grams—a large excess—of finely ground saturating salt was introduced into a cylindrical bottle having a length of approximately 38 cm., a diameter of 10 cm., and a capacity of 3 liters. A known weight of the second salt was then introduced into the bottle and a known weight, 1.5 to 2 liters, of pure solvent added.

The bottles were provided with narrow necks and closed with ground stoppers which were covered by rubber caps when in use. Four bottles were rotated at one time in a horizontal position in a water thermostat. The bottles were rotated initially for sixteen hours at a temperature of 28–30°, after which the temperature was lowered to 25 ± 0.01° and the rotation continued for six hours. The bottles were then set upright without being removed from the thermostat and allowed to settle for four hours or more. Two samples of 500 cc. or more were then removed from each bottle and the amounts of solution determined by weighing in glass-stoppered Erlenmeyer flasks. The solvent was then removed by distillation and the residue containing the salts transferred to a beaker or small dish. The amount of the saturating salt was then determined gravimetrically in all cases. With potassium chloride as the saturating salt the chloride was determined by weighing as silver chloride in a Gooch crucible. With potassium perchlorate as the saturating salt, the potassium was determined as potassium sulfate by adding an excess of sulfuric acid to the residue left by distillation of the solution after transferring it to a silica or platinum dish and heating to constant weight. This method was tested with known mixtures of potassium perchlorate with ammonium salts and found to be sufficiently accurate. The solubility of barium nitrate was determined by weighing the barium as barium sulfate. Due to the very slight solubility of the nitrate and consequent small weight of barium sulfate, the analyses were not very satisfactory. The mean values obtained, however, lie on a fairly smooth curve.

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[8] W. A. Noyes, THIS JOURNAL, 45, 860 (1923).

Experimental Results

The solubilities of the different saturating salts in solutions with known amounts of a second salt are shown in the tables. All concentrations are expressed in moles per liter. The density of the pure solvent was used in calculating the concentrations. In addition, for the purpose of com-

TABLE I

SOLUBILITY OF POTASSIUM CHLORIDE IN THE PRESENCE OF AMMONIUM NITRATE IN ETHYL ALCOHOL AT 25°

Concn. NH_4NO_3 × 10^3	Concn. KCl (anal.) × 10^3			Concn. KCl (mean) × 10^3	$-1/2 \log P_{i_0}/P_i$	$\sqrt{\mu} \times 10^2$
0.000	3.116	3.096	3.111	3.108	0.0000	5.574
.188	3.134	3.115		3.125	.0024	5.755
.466	3.136	3.146		3.141	.0045	5.923
.992	3.341	3.313		3.327	.0295	6.657
2.352	3.716	3.716		3.716	.0775	7.794
4.807	5.038	4.997		5.020	.2082	9.906
8.587	7.233	7.225		7.229	.3665	12.570
19.470	8.818	8.836		8.827	.4534	16.813
51.290	11.160	11.102		11.131	.5540	24.980

TABLE II

SOLUBILITY OF POTASSIUM PERCHLORATE IN THE PRESENCE OF AMMONIUM SALTS IN ETHYL ALCOHOL AT 25°

(a) Added Salt Ammonium Nitrate

Concn. NH_4NO_3 × 10^4	Concn. $KClO_4$ (anal.) × 10^4		Concn. $KClO_4$ (mean) × 10^4	$-1/2 \log P_{i_0}/P_i$	$\sqrt{\mu} \times 10^2$
0.00	5.669	5.640	5.654	0.0000	2.377
2.54	5.996	5.976	5.986	.0254	2.920
4.88	6.198	6.269	6.233	.0425	3.333
9.71	6.743	6.803	6.773	.0786	4.060
18.58	7.255	7.311	7.283	.1089	5.083
43.45	8.441	8.350	8.396	.1712	7.200

(b) Added Salt Ammonium Perchlorate

Concn. NH_4ClO_4 × 10^4					
0.00	5.669	5.640	5.654	0.0000	2.377
2.22	4.910	5.048	4.979	.0252	2.687
5.14	4.088	4.087	4.087	.0425	3.048
10.04	3.288	3.215	3.251	.0690	3.648
17.42	2.563	2.510	2.536	.1005	4.462

(c) Added Salt Ammonium Iodide

Concn. NH_4I × 10^4					
0.00	5.669	5.640	5.654	0.0000	2.377
4.95	6.143	6.154	6.148	.0368	3.331
8.56	6.432	6.554	6.493	.0602	3.883
11.41	6.737	6.831	6.784	.0778	4.264
15.18	7.018	7.118	7.068	.0974	4.717
17.65	6.950	7.362	7.156	.1022	4.971
23.43	7.444	7.480	7.462	.1206	5.557

TABLE III

SOLUBILITY OF BARIUM NITRATE IN THE PRESENCE OF AMMONIUM BROMIDE IN ETHYL ALCOHOL AT 25°

Concn. NH_4Br $\times 10^5$	Concn. $Ba(NO_3)_2$ (anal.) $\times 10^5$	Concn. $Ba(NO_3)_2$ (mean) $\times 10^5$	$-1/3 \log P_{i_0}/P_i$	$\sqrt{\mu} \times 10^2$
0.0	0.91 1.07	0.99	0.0000	0.55
20.3	1.43 1.43	1.43	.1597	1.56
33.0	1.61 1.79	1.70	.2348	1.95
65.8	2.39 1.81	2.10	.3266	2.68

paring with the theory, the square roots of the ionic strengths and the calculated values of $-\ ^1/_2 \log P_{i_0}/P_i$ are given. In the case of the biunivalent salt, barium nitrate, the function used is $-\ ^1/_3 \log P_{i_0}/P_i$.

Discussion

The results in general resemble those in other solvents: there is a uniform increase in solubility on the addition of a salt without a common ion and a decrease on the addition of a salt with a common ion.

The Debye–Hückel theory leads to the equation

$$-\log f = \frac{2.72\, Z_1 Z_2 \sqrt{\mu}}{1 + (0.576 \times 10^8)a\sqrt{\mu}} \tag{1}$$

for ethyl alcohol at 25°, where f is the activity coefficient of the salt, Z_1 and Z_2 are the valences of the ions, a is the average ion diameter and μ the ionic strength. Inasmuch as, for a uni-univalent salt

$$-\log f = -1/2 \log P_{i_0}/P_i - \log f_0 \tag{2}$$

where the quantity P_i indicates the product of the ion concentrations of the salt, P_{i_0} indicates this product for the salt in the pure solvent, and f_0, the activity coefficient of the salt in the pure solvent, is a constant, the values of $-1/2 \log P_{i_0}/P_i$ plotted against the square root of the ionic strengths should give a curve which is very nearly a straight line with a slope of 2.72 for dilute solutions.

Figures 1 and 2 show how the curves from the solubility measurements compare with the limiting line from Equation 1.

Examination of these curves shows considerable deviation from the Debye–Hückel limiting slope. The experimental curves all have a greater slope than the theoretical. This could be accounted for only by assuming negative values of a in (1). The relative deviations from the Debye–Huckel limiting slope are slightly less in the potassium perchlorate solutions than in the potassium chloride solutions where the concentrations are somewhat greater. Comparison of the curves with those obtained for similar solutions in isopropyl alcohol and acetone by Kraus and Seward[5] shows that the relative deviations from the theoretical limiting slope are much less in ethyl alcohol solutions than in isopropyl alcohol and acetone.

It has been pointed out that the treatment of Debye and Hückel in arriving at Equation 1 involves certain approximations which cause considerable error with ions of higher valence in water and even with univalent ions in solvents of low dielectric constant. Gronwall, La Mer and Sandved[9] by calculating the influence of the neglected higher terms of the Debye–Hückel equation have derived corrections to account for such deviations as those observed. Bjerrum,[10] by calculating the probability of the existence of associated ion pairs and treating them as uncharged, was able to explain such deviations while giving reasonable values for ion

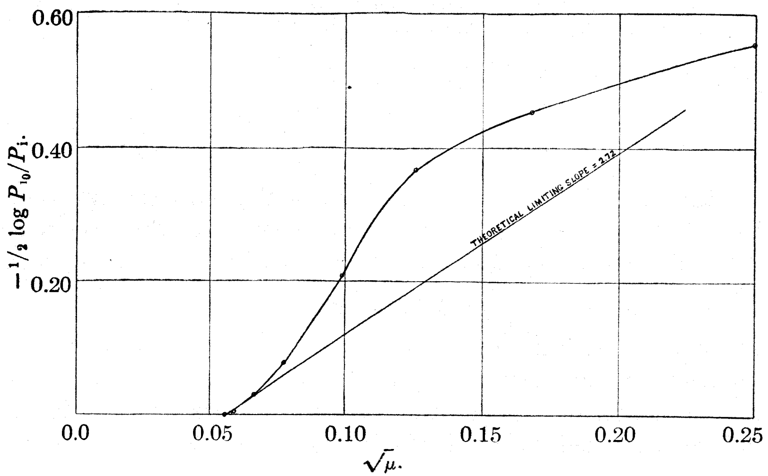

Fig. I.—KCl + NH_4NO_3.

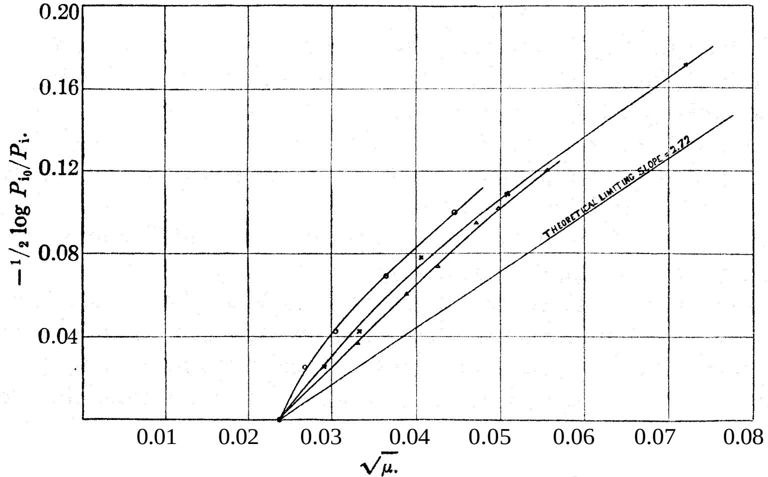

Fig. 2.—0, $KClO_4$ + NH_4ClO_4; ×, $KClO_4$ + NH_4NO_3; △, $KClO_4$ + NH_4I.

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[9] Gronwall, La Mer and Sandved, *Physik. Z.*, 29, 358 (1928).

[10] Bjerrum, *Det. Kgl. Danske Videnskab Selskab, Math.-fys. Medd.*, [9] 7, 1 (1926).

diameters. Both the treatment of Gronwall, La Mer and Sandved and that of Bjerrum lead to the same conclusion, namely, that deviations from the Debye–Hückel limiting slope are to be expected in solutions of lower dielectric constant even in very dilute solutions and the smaller the average ion diameter the greater the positive deviation from the limiting slope.

By applying the results of Bjerrum's calculations a value of 2.5 Å. is obtained for the average ion diameter in the potassium perchlorate–ammonium nitrate mixtures in ethyl alcohol. This appears to be a reasonable value. Moreover, taking different points on the curve, the average diameters obtained are fairly constant.

Summary

The solubilities of potassium chloride, potassium perchlorate and barium nitrate in the presence of other salts in ethyl alcohol have been measured and the results compared with those predicted by the inter-ionic attraction theory.

While the solubility results in ethyl alcohol show marked deviations from those predicted on the basis of the original Debye–Hückel approximation, they seem to be, qualitatively at least, in agreement with the inter-ionic attraction theory as developed by Gronwall, La Mer and Sandved or by Bjerrum.

CAMBRIDGE, MASSACHUSETTS

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

THE FREE ENERGY OF STANNOUS HYDROXYL CHLORIDE AND THE ACTIVITY COEFFICIENT OF STANNOUS CHLORIDE AND STANNOUS ION

BY MERLE RANDALL AND SENZO MURAKAMI

RECEIVED SEPTEMBER 2, 1930 PUBLISHED OCTOBER 6, 1930

The hydrolysis product of stannous ion is the basic stannous hydroxyl chloride $SnOHCl \cdot H_2O$, which is a stable white insoluble solid.[1] The determination of the equilibrium of the hydrolysis reaction

$$Sn^{++} + Cl^- + 2H_2O(l) = SnOHCl \cdot H_2O(s) + H^+; \; K_m = m(H^+)/m(Sn^{++})m(Cl^-) \quad (1)$$

enables us, by combination with the known free energies of the other substances occuring in Equation 1, to determine the free energy of the solid hydrolysis product. Furthermore, from the rather unusual way in which the activity coefficients of H^+ and Cl^- occur in the expression for the equilibrium constant, the individual activity coefficient of the stannous ion

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[1] The simplest formula of the basic salt is used. The amount of hydration is uncertain. See (a) Proust, *J. Phys.*, 61, 338 (1804); Ann. *chim.*, 28, 213 (1798); (b) Davy, *Trans. Roy. Soc.* (London), 102A, 169 (1912); (c) Ditte, *Compt.* rend., 94, 792, 1114 (1882); Ann. chim., [5] 27, 145 (1882); Comfit, rend., 97, 42 (1883).

is obtained by means of assumptions which are less uncertain than those usually employed.

The Solubility of Stannous Hydroxyl Chloride in Aqueous Hydrochloric Acid at 25°.—The stannous hydroxyl chloride was prepared in two ways. (1) In the first series of experiments an approximately 0.5 M solution of stannous chloride was prepared by dissolving c. p. $SnCl_2\cdot2H_2O$ in conductivity water with the addition of just enough c. p. hydrochloric acid (0.006–0.008 M) to give a clear solution. Pure metallic tin was then added. The air was displaced and the solution agitated by a stream of pure nitrogen which was bubbled through. The solution was then added, in the absence of air, to a large volume of air-free conductivity water. The precipitate formed was washed several times by decantation with air-free water. The suspension of the solid in water was used for the solubility experiments. (2) In the remaining experiments the stock solution of acid stannous chloride was precipitated by adding an air-free solution of sodium chloride and hydroxide, the chloride being in large excess. The precipitate was washed free from sodium ion by decantation, as before. On analysis our salt corresponded to the formula $SnOHCl\cdot(1.00 \pm 0.01)H_2O$.

A portion of the paste containing about 10 g. of the solid phase was transferred, in the absence of air, to a 250-ml. pyrex distilling flask body which had been swept free of air by nitrogen. Dilute air-free hydrochloric acid

TABLE I

$Sn^{++} + Cl^- + 2H_2O(l) = SnOHCl\cdot H_2O(s) + H^+$ (25°)

Expt.	Days rotated	Sn^{++}	Cl	H^+	Log K_m	$\mu^{1/2}$	Ratio $HCl/SnCl_2$	1/3Log K_m	Log $\gamma(SnCl_2)$ + const.
1	4	0.02968	0.14020	0.08124	1.289	0.411	2.23	0.430	0.3511
2	6	.03045	.14074	.07985	1.270	.412	2.62	.423	.3449
3	9	.02730	.11558	.06098	1.283	.412	2.23	.428	.3491
4	12	.03140	.15223	.08943	1.274	.423	2.84	.425	.3461
5	15	.01006	.04789	.02777	1.760	.241	2.70	.587	.5280
6	13	.01234	.05602	.03134	1.662	.261	2.58	.554	.4921
7	15	.003261	.01491	.008387	2.237	.135	2.56	.746	.7083
8	16	.002987	.01227	.006290	2.233	.124	2.10	.744	.7103
9	9	.002981	.01225	.006290	2.236	.123	2.10	.745	.7113
10	13	.002802	.01085	.005242	2.237	.117	1.87	.746	.7123
11	11	.002802	.01085	.005242	2.237	.117	1.87	.746	.7123
12	21	.002824	.01089	.005242	2.231	.117	1.86	.744	.7103
13	46	.01176	.07560	.05208	1.770	.296	4.43	.590	.5238
14	5	.01410	.06790	.03970	1.618	.286	2.82	.539	.4738
15	8	.006407	.03294	.02011	1.980	.198	3.12	.658	.6078
16	12	.02329	.10949	.06290	1.392	.360	2.70	.464	.3900
17	9	.008168	.03731	.02097	1.838	.213	2.56	.613	.5587
18	19	.009081	.03879	.02062	1.768	.218	2.21	.589	.5347
19	20	.009248	.03825	.01975	1.747	.218	2.14	.582	.5277
20	45	.009907	.04363	.02382	1.741	.231	2.40	.580	.5230
21	78	.008825	.04023	.02358	1.822	.220	2.66	.607	.5520

solution or water was added, the flasks were sealed and rotated in the thermostat at 25 ± 0.02.[2]

After the time of rotation indicated in Col. 2 of Table I, the solution was filtered[2] and analyzed (moles per 1000 g. of water in vacuum). The stannous-ion constituent (Col. 3) was determined by titration with potassium permanganate solution. Dilute nitric acid was added to give a sufficient hydrogen-ion concentration for the titration. After titration the chloride-ion constituent (Col. 4) was determined as silver chloride by precipitation The hydrogen-ion constituent was determined by difference. In Expts. 7 to 13 in which the stannous ion was very small the hydrogen-ion constituent was determined by titration with sodium hydroxide solution (phenolphthalein indicator) and chloride-ion constituent was taken equal to twice the stannous ion plus the hydrogen-ion constituent.

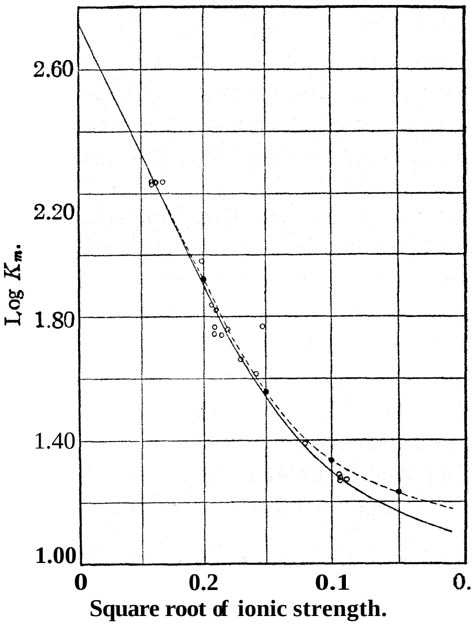

Fig. 1.—$Sn^{++} + Cl^- + 2H_2O(l) = SnOHCl{\cdot}H_2O(s) + H^+(25°)$.

In plotting Fig 1, the scale of the square root of the ionic strength (Cot. 7) was made the same, and the scale of log K (Equation 1, Col. 6) was made one-fourth that of Fig. 2 of Randall and Vietti,[2] for the following reason. If we again consider Equation 1, the expression for the equilibrium constant is

$$K = m\gamma(H^+)/m\gamma(Sn^{++})m\gamma(Cl^-) \qquad (2)$$

The individual activity coefficient of H^+ is very nearly the same as that of Cl^-, especially in the more dilute solutions. Furthermore, we should expect the activity coefficient of these ions to be more nearly alike in mixtures with stannous ion, and in the presence of the large excess of chloride ion.[3] We also find as a consequence of the Debye–Hückel treatment of dilute solutions that at near zero molality[3,4]

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[2] *See* Randall and Vietti, This journal, 50, 1526 (1928).

[3] (a) Bronsted, *ibid.*, 44, 938 (1922); (b) *ibid.*, 45, 2898 (1923); (c) Brönsted and La Mer, *ibid.*, 46, 555 (1924); (d) see Randall and Breckenridge. *ibid.*, 49, 1435 (1927).

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

$$\log \gamma = -z^2 A \mu^{1/2} = -z_1 z_2 A \mu^{1/2} \qquad (3)$$

where z is the valence of an ion, A is a constant $= 0.503$ at 25°, and μ is the ionic strength. In the case of the mean activity coefficient z^2 is replaced by 2 for uni-bivalent salts. In order, therefore, to have the plot of the logarithm of the activity coefficient of a bivalent ion, or its value plus a constant superimpose on our standard plot, we must make the scale one-fourth that of a univalent salt. By comparison with the standard curves2 we find $\log K = 2.75$, or

$$\mathrm{Sn^{++} + Cl^- + 2H_2O(l) = SnOHCl{\cdot}H_2O(s) + H^+};\quad \Delta F^\circ_{298\cdot1} = -3750\ \text{cal.} \qquad (4)$$

Using the values of the free energy of chloride ion given by Randall and Young[5] and the value of —6276 cal. for the free energy of stannous ion[a] we find for the free energy of formation of stannous hydroxyl chloride

$$\mathrm{Sn(s) + {}^1\!/_2Cl_2(g) + 1{}^1\!/_2H_2(g) + O_2(g) = SnOHCl{\cdot}H_2O(s)};$$
$$\Delta F^\circ_{298\cdot1} = -154{,}491\ \text{cal.} \qquad (5)$$

If we assume the individual-ion activity coefficients given by Lewis and Randall,[6] we find at four molalities the values for $\log \gamma\ (\mathrm{Sn^{++}}) + \log K$ indicated on the dotted curve. The values of the activity coefficient of stannous ion found by subtracting $\log K$ from the values of $\log K_m$ are, however, probably more nearly the correct values than those found by using the individual-ion activities which are based on the values in pure hydrochloric acid. The values of the activity coefficient of stannous ion are smaller than those of the alkali earth bivalent ions.

We may also write Equation 1 in the form

$$\mathrm{Sn^{++} + 2Cl^- + 2H_2O(l) = SnOHCl{\cdot}H_2O(s) + H^+ + Cl^-};$$
$$K = m\gamma(\mathrm{H^+})m\gamma(\mathrm{Cl^-})/m\gamma(\mathrm{Sn^{++}})m^2\gamma^2(\mathrm{Cl^-}) \qquad (6)$$

where the numerical value of K is obviously identical with that in Equation 1. We may also write

$$\log K = \log K_m + \log \gamma^2_\pm(\mathrm{HCl}) - \log \gamma^3_\pm\ (\mathrm{SnCl_2})$$

whence, rearranging

$$\log \gamma_\pm(\mathrm{SnCl_2}) + {}^1\!/_3 \log K = {}^1\!/_3 \log K_m + {}^2\!/_3 \log \gamma_\pm(\mathrm{HCl}) \qquad (7)$$

TABLE II

ACTIVITY COEFFICIENT OF STANNOUS CHLORIDE AND OF STANNOUS ION

m	Log $\gamma_\pm(\mathrm{Sn^{++}})$	$\gamma_\pm(\mathrm{Sn^{++}})$	Log $\gamma_\pm(\mathrm{SnCl_2})$	$\gamma_\pm(\mathrm{SnCl_2})$
0.0001	-0.074	0.843	-0.028	0.938
.0010	− .234	.583	− .092	.809
.0025	− .366	.431	− .145	.716
.0050	− .518	.303	− .205	.624
.01	− .726	.188	− .291	.512
.02	-1.002	.0995	− .400	.398
.05	-1.394	.0404	− .548	.283
.1000	-1.554	.0279	− .633	.233

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[5] See Randall and Young, THIS JOURNAL; 50, 989 (1928).

[6] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances." McGraw-Hill Book Co., New York and London, 1923.

The values of log $\gamma_{\pm}$ $(SnCl_2)$ given by this procedure will be those in the presence of hydrochloric acid, and the values of log $\gamma_{\pm}(HCl)$ which should be used are those in the presence of stannous chloride, We give in Table I along with the values of $^1/_3$ log K_m (Col. 9), the values for the ratio of the molality of the hydrochloric acid to that of stannous chloride, and the values of $^1/_3$ log K_m + $^2/_3$ log $\gamma_{\pm}(HCl)$ = log $\gamma_{\pm}(SnCl_2)$ + const., where the value of $^2/_3$ log $\gamma_{\pm}(HCl)$ is taken from the curves of Randall and Breckenridge in mixtures of hydrochloric acid and barium chloride at the same ratio and same ionic strength. This approximation is not entirely justified as the stannous chloride is a "weaker" salt than barium chloride, but the approximation is better than taking the activity coefficient in pure hydrochloric acid. The values of $^1/_3$ log K_m and of $^1/_3$ log K_m + $^2/_3$ log $\gamma_{\pm}(HCl)$ are plotted against $\mu^{1/2}$ in Fig. 2 and lead to an extrapolated value of $^1/_3$ log K which is identical with $^1/_3$ log K, as was found from Fig. 1. The values of log $\gamma_{\pm}(Sn^{++})$ and of log $\gamma_{\pm}(SnCl_2)$ at round molalities, as determined by substituting log K in Equations *2* and 7, are given in Table II.

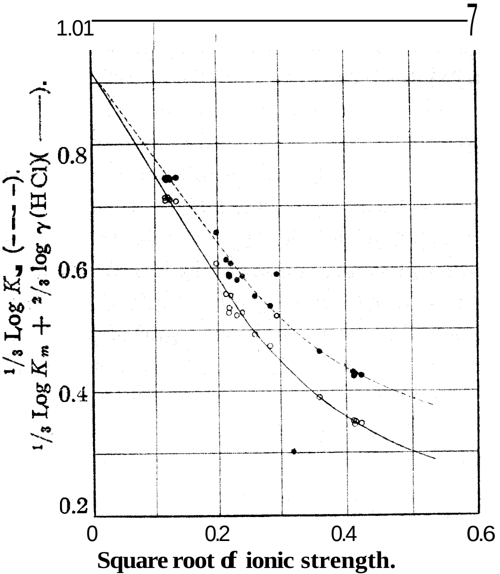

Fig. 2.—$Sn^{++} + 2Cl^- + 2H_2O(l) = SnOHCl \cdot H_2O(s) + H^+ + Cl^-(25°)$.

Summary

The equilibrium in the hydrolysis of stannous chloride has been measured at 25°. The free energy of the solid stannous hydroxyl chloride and the activity coefficient of stannous chloride and of stannous ion have been calculated,

Berkeley, California

NOTES

The Molecular Diameters of Nitrogen Pentoxide.—Eyring and Van Valkenburgh[1] have just published a determination of the viscosity of nitrogen pentoxide; from this viscosity they calculate a molecular diameter of 8.53×10^{-8} cm. I should like to make a few comments on the application of this value to reaction rate calculations. It is common to all modern theories of unimolecular reaction that the rate of production of activated molecules is calculated by assuming that it is equal to the rate at which these activated molecules would enter into collision if they were present at the Maxwell–Boltzmann equilibrium concentration. In this usage a collision is an interaction which leads to a redistribution of internal energy; the diameter which is appropriate to the calculation of the number of such collisions is not the ordinary kinetic theory diameter, though it must be of the same order of magnitude, if grave difficulties are to be avoided. Thus the 8.53×10^{-8} cm. of Eyring and Van Valkenburgh is of no *direct* significance for the theory of the unimolecular decomposition of nitrogen pentoxide.

The statement of Eyring and Van Valkenburgh that recent calculations[2] show that a diameter of 6×10^{-6} cm. must be used to obtain sufficient activations is hardly correct. When these calculations were made, three years ago, they referred to the particular form of theory proposed by Fowler and Rideal.[3] Since that time more satisfactory theories have been proposed, and also considerable new work has been done on the actual measurement of the reaction rate at low pressures.[4] It now appears that the true homogeneous reaction rate falls off to half its high-pressure value at about 0.005 mm. Reference to the calculations made by the writer[5] before these new data were available shows that, on one particular form of theory, they may be accounted for by using a diameter of about 17×10^{-8} cm., which must be considered a permissible value. The details of the theory are so uncertain that one cannot assert the true diameter for collisional deactivation to be greater than that determined by Eyring and Van Valkenburgh; there is, however, no reason why it should not be.

CONTRIBUTION FROM THE
GATES CHEMICAL LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA
LOUIS S. KASSEL[6]

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PUBLISHED OCTOBER 6, 1930

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[1] Eyring and Van Valkenburgh, THIS JOURNAL, 52, 2619 (1930).

[2] Tolman, Yost and Dickinson, *Proc. Nat. Acad. Sci.*, 13, 188 (1927); B. Lewis, *Science*, 66, 331 (1927).

[3] Fowler and Rideal, *Proc. Roy. Soc.* (London), 113A, 570 (1927).

[4] Ramsperger, Nordberg and Tolman, *Proc. Nat. Acad. Sci.*, 15, 453 (1929); Ramsperger and Tolman, ibid., 16, 6 (1930); Schumacher and Sprenger, *ibid.*, 16, 129 (1930); Hibben, *J. Phys. Chem.*, 24, 1387 (1930).

[5] Kassel, *ibid.*, 32, 1065 (1928).

[6] National Research Fellow.

Note on Bimolecular Reactions.—In homogeneous bimolecular reactions, integration of the two velocity expressions, $dx/dt = k(a - x)^2$, when the two reacting molecules are alike or of the same initial concentrations, and $dx/dt = k(a - x)(b - x)$, when the reacting molecules are unlike, leads to the following familiar equations

$$k = \frac{1}{ta} \times \frac{x}{(a - x)}, \text{ and} \tag{1}$$

$$k = \frac{1}{t(a - b)} \times \log \frac{b(a - x)}{a(b - x)} \tag{2}$$

where the symbols have their usual significance. It is a physical necessity that expression (2) reduce to (1) if $b = a$. Yet it is obvious that (2) assumes the form 0/0 when $b = a$.

It has been shown in several places[1] that (2) does become equal to (1) under this condition, by expanding the logarithm term in (2) in series and evaluating the resulting expression. However, the methods quoted require a page or more of mathematical simplification to obtain the desired result. On the other hand, making use of the customary way of evaluating 0/0, we have been able to find in a very simple manner the limiting value of the ratio as $b \longrightarrow a$, and from this to show the identity of the two expressions. It proves to be a rather interesting situation, and since it does not appear in any of the ordinary textbooks on the subject, we thought that it might be worth while to pass it on.

From (2)

$$k = \frac{\log b + \log (a - x) - \log a - \log (b - x)}{t(a - b)} = \frac{0}{0}$$

when $b = a$. Now since this would be 0/0 for all finite values of x and t, for our purpose we may treat these as constants and take

$$\lim_{b \longrightarrow a} \frac{f(b)}{F(b)}$$

Treating b as the variable, and differentiating numerator and denominator separately[2] we get[a]

$$\frac{\frac{1}{b} - \frac{1}{b - x}}{-t}$$

---

[1] See, for example, Nernst and Schönfliess, "Einführung in die mathematische Behandlung der Naturwissenschaften," Oldenbourg, Munich. 1923, p. 262 *et seq.*; Taylor. "Treatise on Physical Chemistry," D. van Nostrand Company, New York, 1925, p. 869.

[2] See any standard calculus book for explanation of rule to evaluate 0/0, such as Wilson, "Advanced Calculus." Ginn and Co., 1921, p. 61, or Love, "Calculus," The Macmillan Company, 1921, p. 204.

[3] Although b was constant in the original differential equation, we are considering here the special case when $b \longrightarrow a$, that is, variation in b's value.

and on simplifying = $x/tb(b - x)$. This, of course, when $b = a$, becomes $x/ta(a - x)$, which is expression (1).

CONTRIBUTION FROM THE
GEORGIA SCHOOL OF TECHNOLOGY
ATLANTA, GEORGIA
H. B. FRIEDMAN
H. K. FULMER

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

THE SKRAUP REACTION WITH CERTAIN AZO COMPOUNDS

BY KONOMU MATSUMURA

RECEIVED FEBRUARY 27, 1930 PUBLISHED OCTOBER 6, 1930

In the course of an investigation of the possible explanation of the reaction mechanism of the formation of p-phenanthroline in the Skraup reaction with p-aminoresorcin dimethyl ether, p-benzene-azo-resorcin dimethyl ether was subjected to the Skraup reaction and the product was found unexpectedly to be also p-phenanthroline; the yield in this case was three times as good as in the same reaction with p-aminoresorcin dimethyl ether. The formation of *p*-phenanthroline was also established, in the same way, from *p*-benzene-azo-resorcin, whereas from p-aminoresorcin, no crystalline matter could be isolated, on working under the same conditions.

From these facts it seemed that in case of the Skraup reaction with rather unstable amines, better results might follow if the corresponding azo compounds were used as reactants: and here I have extended this study to several azo compounds.

Concerning the study of the Skraup reaction with azo compounds, work has been reported by Claus and Stegelitz[1] and later by Lellmann and Lippert.[2] They established the formation of the corresponding ring compounds in this reaction, but the yield in each case was reported to be very poor. In the present investigation the reactions were carried out with the addition of arsenic acid, this being the only difference from the methods of previous investigations.

TABLE I

EFFECT OF ARSENIC ACID IN THE SKRAUP REACTION WITH AZO COMPOUNDS

Reactants	Products	Yield, g.	
		Presence of H_3AsO_4	Absence of H_3AsO_4
Azobenzene, 10 g.	Quinoline picrate	0.5	0.65
	6,6′-Diquinolyl	5.7	1.2
p-Benzene-azo-resorcin dimethyl ether	Quinoline	2.0–2.5	1.4
	p-Phenanthroline	1.35–1.5	0.3

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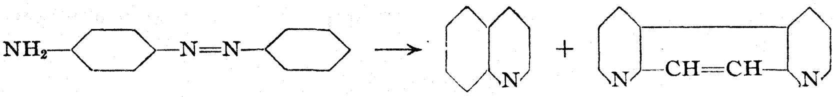
[1] Claus and Stegelitz, *Ber.*, 17, 2380 (1884).

[2] Lellmann and Lippert, *ibid.*, 24, 2623 (1891).

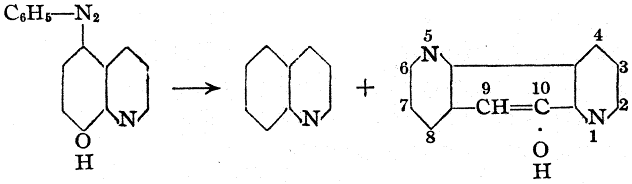
First of all, in order to find the influence of the presence of arsenic acid in the reaction, the following two pairs of experiments were performed for the sake of comparison, with the result that, in the Skraup reaction with azo compounds, the presence of arsenic acid gave far better yields (Table I).

In view of this fact, it seems that the action of arsenic acid in the Skraup reaction may be other than it has previously been thought to be. In the Skraup reaction with p-amino-azobenzene, p-phenanthroline could he isolated in a satisfactory yield in accordance with the scheme



The preparation of p-phenanthroline was reported by Kaufmann and Radošević[3] by the Skraup reaction with 6-aminoquinoline and recently by Smith by the same reaction with *p*-phenylenediamine.[4] The Skraup reaction with p-amino-azobenzene, however, appears to be the most suitable for preparing it in quantity, because *p*-amino-azobenzene is more easily accessible than 6-amonoquinoline or *p*-phenylenediamine.

In the Skraup reaction with benzene-azo-5-hydroxy-8-quinoline, the yield of 10-hydroxy-*m*-phenanthroline was very poor on working up under a variety of conditions.



La Coste,[5] in the Skraup reaction with *m*-nitraniline, could isolate an hydroxy-m-phenanthroline (m. p. 159–60°) as a by-product and, as to the position of the hydroxyl group, he concluded, under his reasonable interpretation, that the substance might be 2-hydroxy-m-phenanthroline.

The hydroxy-m-phenanthroline he had obtained appears to be very near in its properties to 10-hydroxy-m-phenanthroline (m. p. 157–158°), which I have now obtained.

Pictet and his co-worker[6] obtained phenotripyridine in good yields in the Skraup reaction with 1,3,5-triaminobenzene. Chrysoidin was now submitted to the Skraup reaction, with the expectation of obtaining one of its structural isomers in accordance with the equation

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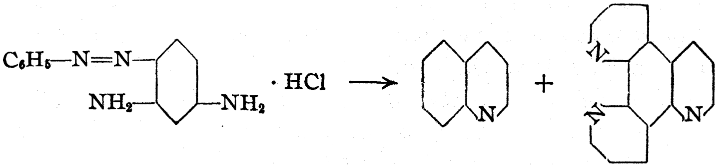
[3] Kaufmann and Radošević, *Ber.*, 42, 2612 (1909).

[4] Smith, This Journal, 52, 397 (1930).

[5] La Coste, *Ber.*, 16, 674 (1883).

[6] Pictet and Barbier, *Bull. soc. chim.*, [3] 13, 28 (1895).



After a tedious process of separation, a minute amount of colorless needles (m. p. 155–156°) could be isolated by means of petroleum ether but the scarcity of the material has rendered its further characterization impossible.

Experimental

General Procedure for the Skraup Reaction with Azo Compounds.—A mixture of monoazo compound ($^1/_{20}$ mole), glycerin (18 g.), concd. sulfuric acid (18 g.) and arsenic acid (9 g.) was gently refluxed in an oil-bath (bath temperature 160–195°) for two to thirty hours. The flask contents, which consisted of a hard black lump on cooling, was digested with hot water and the filtered liquid, after being made alkaline, was distilled with steam. The distillate was shaken with ether. On evaporating the solvent, after thorough drying with sodium sulfate, quinoline could be isolated. It was identified by converting it into its picrate.

From the residue of the steam distillation, by means of benzene, another component of the products could be isolated. Further purification was effected by recrystallization of its sulfate from hot alcohol.

In the case of 10-hydroxy-*m*-phenanthroline, instead of benzene extraction, the material was extracted first with cold alcohol, then with benzene, ether and petroleum ether successively.

TABLE II

SKRAUP REACTIONS

Reactant	G.	Reaction time, hrs.	Products	Yield, g.
1 p-Benzene-azoresorcin dimethyl	10	21	Quinoline	2.5
1 ether			*p*-Phenanthroline	1.5
2 p-Benzene-azoresorcin	8.85	15	Quinoline	2.3
2			*p*-Phenanthroline	0.07
3 Azobenzene	10	15	Quinoline picrate	0.5
3			6,6′-Diquinolyl	5.7
4 p-Amino-azobenzene	10	30	Quinoline	2.5
4			*p*-Phenanthroline	7.7
5 *p*-Nitrobenzene-azo-4-naphthol-1	15	21	*p*-Phenanthroline	3 2
6 *p*-Chlorobenzene-azo-phenol	10	21	6-Chloroquinolie	5.2
7 Benzene-azo-5-hydroxy-8-quino-	15	2	Quinoline	2.6
7 line			**10-Hydroxy-m-phenanthroline**	0.25
8 Chrysoidine	20	3	Quinoline	2.5
			Minute amount of crystals	..

TABLE II (*Concluded*)

Compound	Properties	M. p., °C.
1 Quinoline picrate	Citron yellow needles from benzene	203
1 *p*-Phenanthroline	Colorless needles from benzene	173
2 Quinoline picrate	......	203
2 *p*-Phenanthroline	......	173
3 Quinoline picrate	......	203
3 6,6′-Diquinolyl	Colorless plates of silky luster from dilute alcohol	179–180
4 Quinoline picrate	......	203
4 *p*-Phenanthroline	......	173
5 *p*-Phenanthroline	......	171–172
6 6-Chloroquinoline	Colorless prisms from benzene	41–42
picrate	Yellow hair-like needles from acetone	217
7 Quinoline picrate	......	203
7 10-Hydroxy-*m*-phenanthroline	Colorless needles from benzene. Soluble in dil. HCl and NaOH. Ferric chloride reaction is dark violet	157–158
8 Quinoline picrate	......	203
8 Minute amt. crystals	Colorless needles from petroleum ether. Soluble in dil. HCl	155–156

Compound	Carbon, %		Hydrogen, %		Nitrogen, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
1 Quinoline picrate	50.28	50.35	2.79	2.85	15.64	15.75
1 p-Phenanthroline	80.00	80.19	4.44	4.72	15.56	15.61
2 *p*-Phenanthroline					10.94	10.91
3 6-6'-Diquinolyl	84.38	84.58	4.69	4.96	15.56	15.74
4 *p*-Phenanthroline	80.00	79.85	4.44	4.49	15.56	15.31
5 p-Phenanthroline	80.00	80.12	4.44	4.66	15.56	15.76
6 6-Chloroquinoline picrate	45.86	46.06	2.29	2.53	14.27	14.03
7 10-Hydroxy-m-phenanthroline	73.47	73.63	4.08	4.43	14.29	14.02

TABLE III

DERIVATIVES OF 10-HYDROXY-*m*-PHENANTHROLINE

	Formula	Properties	Water of crystallization		Analysis	
			Calcd.	Found	Calcd.	Found
Sulfate	$C_{12}H_8ON_2$, H_2SO_4	Yellow needles from alc., m. p. 273° (dec.); easily sol. in water				
Chloroplatinate	$[C_{12}H_8ON_2(HCl)_2]\cdot PtCl_4\cdot 1^1/_2H_2O$	Yellow needles from dil. HCl, m. p. 309°	4.27	4.28	C, 23.76 H. 1.66 Pt, 32.21	C, 23.92 H, 2.04 Pt, 31.21
Picrate	$C_{12}H_8ON_2\cdot C_6H_3O_7N_3$	Yellow needles from alc., m. p. 237° (dec.)			N, 16.47	N, 16.75

I desire to express my best thanks to Professor Hata for the interest which he has kindly taken in this work.

Summary

1. It has been reported that in the Skraup reaction with azo compounds, the presence of arsenic acid gives better results.

2. In connection with this fact, the following quinoline compounds have been prepared; quinoline, *p*-phenanthroline, 6,6′-diquinolyl, 6-chloroquinoline and 10-hydroxy-m-phenanthroline, of which the last is a new compound.

TOKYO, JAPAN

[CONTRIBUTION FROM THE DEPARTMENT FOR DISEASES OF THE CHEST, JEFFERSON HOSPITAL]

MERCURY DERIVATIVES OF ACETYLAMINOCRESOLS[1]

BY A. PROSKOURIAKOFF AND R. J. TITHERINGTON

RECEIVED APRIL 23, 1930 PUBLISHED OCTOBER 6, 1930

Introduction

Organic compounds of mercury have gained considerable prominence during the last few years in the field of pharmaceutical chemistry as general antiseptics. In almost every field of application, they have displaced their inorganic precursor, mercuric bichloride, and have established for themselves a very important position among modem synthetic drugs. The value of the new organic mercurials in the treatment of syphilis and the importance of their use in conjunction with the well-known arsenicals are at present well recognized. Further investigation in this field, however, seemed to be especially desirable in view of the fact that comparatively few organic mercury compounds suitable for therapeutic use have been synthesized and still fewer were thoroughly studied and tried clinically. Among these, phenol derivatives and dyestuffs were given much attention and large groups of their mercury derivatives were synthesized and investigated therapeutically.

In 1906 Hantsch and Auld[2] prepared mercury derivatives of various nitrophenols. In 1919 Schamberg, Kolmer and Raiziss[3] studied the toxicity and bactericidal effect of mercurated nitrophenols and found that sodium hydroxymercury-o-nitrophenolate exhibited interesting therapeutic properties. Later, Raiziss and Proskouriakoff[4] synthesized a number of mercury derivatives of nitrophenols, nitroresorcinols and nitrosalicylic acids for their chemotherapeutic study, assuming that nitro groups enhance the bactericidal influence and the stability of the organic mercurials. Most of the compounds prepared were amorphous and analyses indicated that they were mixtures of mono- and di-mercury compounds and were separable only with considerable difficulty. Of the dyestuff group, mercury derivatives of phthaleins and azo dyes were more thoroughly investigated and some valuable germicidal compounds were discovered, in the first group mentioned. The di-sodium salt of dibromo-hydroxymercurifluorescein is the most successful of this group.[5] In 1925 Proskouriakoff and Raiziss[6]

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[1] Financial assistance in this work has been received from the C. Mahlon Kline Fund.

[2] Hantsch and Auld, *Ber.*, 39, 1105 (1906).

[3] Schamberg, Kolmer and Raiziss, J. *Infectious Diseases*, *24*, *547* (1919).

[4] Raiziss and Proskouriakoff, THIS JOURNAL, 44, 787 (1922).

[5] E. C. White, *ibid.*, 42, 2359 (1920); Young, White and Swartz, J. *Am. Med. Assn.*, 73, 1483 (1919).

[6] Proskouriakoff and Raiziss, THIS JOURNAL, 47, 1974 (1925).

prepared and studied a group of azo dyestuffs and found that mercury can be detoxicated considerably by modifying the organic compound to which it is attached. Mercury derivatives of nitrocresols were studied by Raiziss, Proskouriakoff and Fisher[7] and among them the mono-mercury derivative of 6-nitro-o-cresol and the di-mercury derivative of 5-nitro-o-cresol were found to possess superior germicidal properties.

Several isomers of aminocresols were prepared and mercurated by the authors. These compounds, however, were amorphous and their sodium salts, as one would expect, were not sufficiently stable in solution, depositing on standing a fine gray powder of metallic mercury. The instability of mercurated aminocresols was probably due to the presence of the open amino groups, and the protection of these groups seemed to be desirable in order to render the compounds more stable. It would also diminish the possibility of mercury reacting directly with the amino groups, forming the complex and still more unstable compounds.

With this in mind, the authors undertook the preparation and subsequent mercuration of different isomers of acetylaminocresols. On studying the literature we were unable to find any data on properties and methods of preparation of certain amino- and acetylaminocresols. Some, apparently, never have been prepared. Most of those that have been known were prepared by reducing the corresponding nitrocresol with zinc or tin and hydrochloric acid[8] and acetylating the amino compound thus obtained by boiling it with acetic anhydride in an acetic acid solution.[9] This method of reduction was long and tedious, as it involved the precipitation of the metal and evaporation of the solution for the precipitation of the amino compounds. The yield in our hands was very poor. The acetylation of the aminocresols in glacial acetic acid medium in many cases also presented considerable difficulty, due to the ready solubility of acetylaminocresols in dilute acids, and the yields obtained were very poor, also.

Our attempts to find a better and simpler method for the preparation of aminocresols gave us very satisfactory results when we tried to reduce the nitrocresols with sodium hydrosulfite in alkaline solution. After some experimentation we have adopted the following procedure. The nitrocresol was dissolved in dilute alkali and the boiling solution was then treated with small portions of solid sodium hydrosulfite until the liquid became colorless or slightly yellow. The theoretical amount of hydrosulfite was required. The solution was then cooled and the amino compound came down in almost pure crystalline form, which, after a single

[7] Raiziss, Proskouriakoff and Fisher, paper read at the spring meeting of the American Chemical Society in Washington, D. C., 1924.

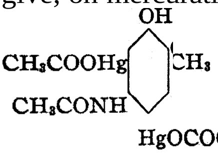
[8] (a) Nolting and Collin, *Ber.*, 17, 270 (1884); (b) Nolting and Kohn, *ibid.*, 17, 367 (1884).

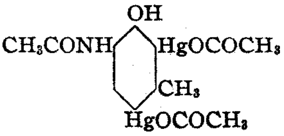
[9] Massen, *ibid.*, 17, 609 (1884).

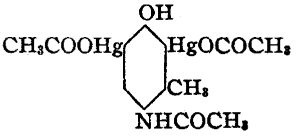
crystallization from water or dilute alcohol, was obtained as a perfectly pure compound suitable for our purposes. The method of the preparation of acetylated aminocresols was considerably improved by carrying on the reaction in aqueous medium. This is a very quick and simple method; the water medium fully protects the hydroxy groups from being involved in the reaction, even though an excess of acetic anhydride be used. The final product is pure and the yield excellent.

The aminocresol is suspended in a small amount of water and treated with a slight excess of acetic anhydride by shaking it for a few minutes in a glass-stoppered Erlenmeyer flask. The compound goes into solution and the acetyl derivative quickly crystallizes on cooling. The acetylaminocresols are thus obtained in a very pure state after the first crystallization.

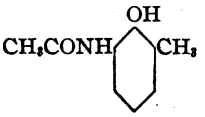
The mercuration of the aminocresols was carried out by treating an alkaline solution of acetylaminocresol with a solution of mercuric acetate in dilute acetic acid solution. The final acid concentration of the solution is in this case an important factor in obtaining uniform yields of a pure crystalline compound of definite structure. The crystalline diacetoxymercury derivatives, apparently, partly hydrolyze on heating in a neutral or insufficiently acid solution, turning into the corresponding amorphous hydroxy-mercury compounds. On boiling with water the compounds produce highly colloidal solutions, acid to litmus. All the compounds were obtained from the reaction mixtures in the form of beautifully uniform crystals of high purity. They were recrystallized once from a 10% solution of acetic acid, dried at 110° in the oven and analyzed for nitrogen and mercury. The analyses showed that in the isomers of acetylaminocresols with ortho and para positions to hydroxyl open, mercury always enters all the positions thus open, leaving the meta positions unsubstituted. Thus 5-acetylamino-o-cresol, 6-acetylamino-m-cresol and 4-acetylamino-m-cresol give, on mercuration, dimercurated compounds







We have attempted to mercurate, with excess of mercuric acetate, 6-acetylamino-o-cresol, which has only para position to hydroxyl open, both ortho positions being already occupied **(A).** As a result we have obtained a good yield of crystalline mono-mercury derivative identical with that



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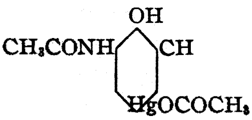

B

obtained by mercuration of this compound with the theoretical amount of mercuric acetate (one mole) (B).

All the mercurated acetylaminocresols prepared by us are soluble in dilute solutions of alkalies. The results of the investigation of their therapeutical activity will be published elsewhere.

The mercury in these compounds was determined by decomposing the compounds with sulfuric acid and potassium permanganate and estimating mercury gravimetrically as sulfide.

Experimental Part

Preparation of 5-Amino-*o*-cresol.—Thirty-four grams of **5-nitro-*o*-cresol** (m. p. 117°) was dissolved in 600 cc. of a 3% solution of sodium hydroxide. The solution was brought to boiling and to the boiling solution was gradually added in small portions about 135 g. of sodium hydrosulfite. The reduction was completed when the solution was almost colorless and the addition of sodium hydroxide to a portion of it gave no red color. The solution was then filtered hot and allowed to cool for twenty-four hours. The crystalline precipitate was then filtered off, washed with a small amount of ice-cold water and dried in a desiccator. It could then be recrystallized from water, giving plates of m. p. 161°.

Preparation of 5-Acetylamino-*o*-cresol.—Eight grams of 5-amino-*o*-cresol (m. p. 161°) was suspended in 150 cc. of water in a glass-stoppered Erlenmeyer flask. To this was added 20 cc. of acetic anhydride and the flask was shaken for about a half hour. It was then cooled and allowed to stand for four hours. The precipitate was filtered off, washed with water and dried in the oven at about 70°; yield, 9.5 g. (88%). The compound was then recrystallized from 350 cc. of 50% ethyl alcohol; yield. 8 g. It can also be purified by dissolving it in dilute alkali and precipitating the compound from the filtered solution by dilute hydrochloric acid. It gives colorless crystals (prisms); melting point, 225°. It is soluble in dilute alkalies and hot water.

Preparation of **4,6-Diacetoxymercuri-5-acetylamino-*o*-cresol.**—Two grams of 5-acetylamino-*o*-cresol (m. p. 225°) was dissolved in 50 cc. of water and 15 cc. of a 4% solution of sodium hydroxide. To this was added 7.8 g. of mercuric acetate dissolved in 60 cc. of warm 15% acetic acid. The whole was warmed until the precipitate dissolved. The solution was then cooled. A voluminous white precipitate formed which under the microscope appeared as colorless long needles radiating from centers.

The compound was washed with a small amount of cold water and dried in the oven at 110° for twelve hours; yield, 4.5 g. It is soluble in dilute alkali, sodium carbonate, glacial acetic acid and dilute acetic acid (on warming). It is insoluble in methyl alcohol, benzene, ether and ethyl acetate. The compound darkens and apparently begins to decompose at about 210°.

Anal. Calcd. for $C_{13}H_{15}O_6NHg_2$: Hg, 50.80; N, 2.05. Found: Hg, 59.10; N, 2.03.

Preparation of 6-Amino-*o*-cresol.—Twenty-five grams of 6-nitro-*o*-cresol was dissolved in 500 cc. of 3% solution of sodium hydroxide. The solution was heated to 90°, heating was discontinued and with rapid stirring solid sodium hydrosulfite was added in 2-g. portions at such a rate as to keep the temperature below 100°. The reduction was completed when 100 g. of sodium hydrosulfite had been added. Five grams of norit was then added and stirring was continued for a few minutes. The solution was filtered and the filtrate was cooled in ice water. The crystallized compound was filtered off and dried in the oven at 60°.

The crude dry compound was recrystallized from carbon tetrachloride. Colorless plates were obtained from water. It is soluble in methyl and ethyl alcohol, acetone, ether, chloroform, hot water, hot benzene and hot carbon tetrachloride; insoluble in petroleum ether; m. p. 89° (uncorr.). It gives a red color with ferric chloride.

Anal. Calcd. for C_7H_9ON: N, 11.38. Found: N, 11.25, 11.27.

The hydrochloride was obtained by dissolving the amino compound in dilute hydrochloric acid and precipitating the hydrochloride by adding an equal amount of concentrated hydrochloric acid (colorless crystals).

Preparation of **6-Acetylamino-*o*-cresol.**—Six grams of 6-amino-o-cresol (m. p. 89°) was suspended in 200 cc. of water in a glass-stoppered Erlenmeyer flask. To this was added 4 cc. of acetic anhydride and the mixture was shaken vigorously. A dark solution resulted which with continued shaking quickly became lighter in color with the separation of dark semi-solid substance. This was filtered off and the filtrate was cooled in ice water. The 3-acetylamino-o-cresol crystallized with the help of stirring and scratching. The crystals were filtered off, washed with water and dried in the oven at 60°.

The compound recrystallized from carbon tetrachloride melted at 78–79° (uncorr.) (long prisms). It is soluble in methyl and ethyl alcohol, acetone, benzene, chloroform, ether, hot water and hot carbon tetrachloride; insoluble in petroleum ether. It gives a blue color with ferric chloride. (The corresponding amino compound gives a red color with the same reagent.)

Anal. Calcd. for $C_9H_{11}O_2N$: N, 8.49. Found: N, 8.36, 8.35.

Preparation of **4-Acetoxymercuri-6-acetylamino-*o*-cresol.**—Two grams of 6-acetylamino-o-cresol was dissolved in 20 cc. of 3% solution of sodium hydroxide. To the warm solution was added 4 g. of mercuric acetate dissolved in 30 cc. of 15% warm acetic acid.

The mixture was heated over a low flame until the precipitate formed at first redissolved. The hot solution was filtered and then cooled in ice water. The crystalline precipitate was filtered off, washed with a little 10% acetic acid and then with water and dried in the oven at 60°; yield, 2.2 g. It can be recrystallized from 10% acetic acid. The compound is soluble in dilute alkalies, acetone, ethyl and methyl alcohol and dilute acetic acid. It is insoluble in benzene, ether and carbon tetrachloride. It melts at 122'.

Anal. Calcd. for $C_{11}H_{13}O_4NHg$: Hg, 47.34; N, 3.31. Found: Hg, 47.42, 47.68; N, 3.26.

Preparation of **6-Amino-*m*-cresol.**—Ten grams of 6-nitro-m-cresol (m. p. 56°) was dissolved in 225 cc. of a 3% solution of sodium hydroxide and the boiling solution was treated with small portions of solid sodium hydrosulfite (about 40 g.) until the solution became almost colorless and a portion of it in a test-tube did not give a red color with sodium hydroxide. It was then allowed to cool, whereupon an amino compound crystallized out. It was filtered off and recrystallized from 50% ethyl alcohol; yield, 4.8 g.

It forms colorless long prismatic needles which melt with decomposition at 162'. An aqueous solution of the compound gives with ferric chloride a red color, while the corresponding nitrocresol and acetylaminocresol do not give this reaction.

The compound is soluble in hot water, dilute acids, methyl and ethyl alcohol, acetone, benzene and ether. It is insoluble in petroleum ether.

Anal. Calcd. for C_7H_9ON: N, 11.38. Found: N, 11.27.

Preparation of **6-Acetylamino-*m*-cresol.**—Five grams of 6-amino-m-cresol was suspended in 75 cc. of water and treated with 7 cc. of acetic anhydride in a glass-stoppered Erlenmeyer flask. The change occurred almost immediately; all went into solution and soon after the precipitate came down. The flask was shaken for about a half hour and then well cooled with ice water. The precipitate was then filtered off, washed with cold water and dried in the oven at about 70°; yield, 5 g.

The compound, recrystallized from 50% ethyl alcohol, forms colorless hexagonal plates. It melts at 171° (uncorr.).

The solution of 6-acetylamino-m-cresol gives no color with ferric chloride. (By this reaction it can be distinguished from the corresponding aminocresol.) It dissolves in alkali with a bluish-green color.

The compound can be dissolved in sodium hydroxide or sodium carbonate and precipitated from the solution by neutralizing it with acetic or hydrochloric acid. It is soluble in hot water, easily soluble in methyl and ethyl alcohol and acetone, much less so in benzene and ether. It is insoluble in petroleum ether and carbon tetrachloride.

Anal. Calcd. for $C_9H_{11}O_2N$: N, 8.49. Found: N, 8.38.

Preparation of **2,4-Diacetoxymercuri-6-acetylamino-*m*-cresol.**—Ten and one-half grams of 6-acetylamino-m-cresol (m. p. 171°) was dissolved in 250 cc. of a 1.5% solution of sodium hydroxide. To this was added, with stirring, a hot solution of 40.2 g. (2 moles) of mercuric acetate in 210 cc. of 20% acetic acid.

The whole was then warmed until the precipitate formed went into solution. The solution was then cooled and allowed to stand for twelve hours. The precipitate was filtered off, washed with water, alcohol and ether and dried in the oven at 60°. This yellowish crystalline precipitate was recrystallized from 10% acetic acid, whereupon colorless long needles were obtained.

The compound dissolves in dilute alkalies, forming a colorless solution. It melts with decomposition at 178°. It was dried in the oven at 110° for fifteen hours and analyzed.

Anal. Calcd. for $C_{13}H_{15}O_6NHg_2$: Hg, 58.80; N, 2.05. Found: Hg, 58.70; N, 2.01.

Preparation of **4-Amino-*m*-cresol.**—Sixteen grams of 4-nitro-m-cresol (m. p. 129°) was dissolved in 350 cc. of a 3% solution of sodium hydroxide. To the boiling solution was gradually added 65 g. of solid sodium hydrosulfite. The reduction was completed when the solution became almost colorless and the amino compound began to precipitate. The mixture was then well cooled, the precipitate filtered off and recrystallized from 100 cc. of 50% ethyl alcohol; yield, 7 g.; colorless prisms, m. p. 179°. Nolting and Kohn[8b] give the melting point for this compound as 174°.

Preparation of **4-Acetylamino-*m*-cresol.**—Six grams of 4-amino-m-cresol (m. p. 179°) was suspended in 50 cc. of water in a glass-stoppered Erlenmeyer flask. To this was added 10 cc. of acetic anhydride and the mixture vigorously shaken. The aminocresol went into solution. On cooling a crystalline precipitate of acetylaminocresol came down. This was filtered off, washed with cold water and recrystallized from water; yield, 5 g. of needles. The compound when dried in the oven at 110° for six hours melts at 130° (incorr.). Staedel and Kolb[10] give for this compound (free from water of crystallization) m. p. 125°. It can be dissolved in dilute alkali and reprecipitated by acidifying with hydrochloric acid.

Preparation of **2,6-Diacetoxymercuri-4-acetylamino-*m*-cresol.**—Two grams of 4-acetylamino-*m*-cresol (m. p. 130°) was dissolved in 20 cc. of a 3% solution of sodium hydroxide. To the warm solution was gradually added, with stirring, a solution of 7.7 g. of mercuric acetate in 30 cc. of 15% acetic acid. The mixture was allowed to stand in a cool place for twenty-four hours. The white crystalline precipitate was filtered off, washed first with cold water, then with alcohol and finally with ether and dried in the air. It was recrystallized from 10% acetic acid and dried at 110° for fifteen hours; yield, 3 g. of colorless crystals (prisms). On heating; in the melting point tube,

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[10] Staedal and Kolb, Ann., 259, 217 (1890).

the compound darkens and gradually decomposes, but does not melt below 250°. It is soluble in dilute alkalies. The solutions are colorless.

Anal. Calcd. for $C_{13}H_{16}O_6NHg_2$: Hg, 58.80; N, 2.05. Found: Hg, 58.69; N, 2.06.

Summary

1. A simple method of preparation of aminocresols from corresponding nitrocresols by reduction with sodium hydrosulfite is described.

2. 6-Amino-o-cresol, 6-acetylamino-o-cresol, 6-amino-m-cresol and 6-acetylamino-m-cresol were prepared and studied.

3. The following mercury derivatives of acetylaminocresols were synthesized and studied: 4-acetoxymercuri-6-acetylamino-o-cresol, 4,6-diacetoxymercuri-5-acetylamino-o-cresol, 2,4-diacetoxymercuri-6-acetylamino-m-cresol and 2,6-diacetoxymercuri-4-acetylamino-*m*-cresol.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

BENZOHYDRYLMAGNESIUM CHLORIDE AND THE APPARENT PRIOR FORMATION OF FREE BENZOHYDRYL RADICALS

BY HENRY GILMAN AND E. A. ZOELLNER

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Introduction

In the preparation of all Grignard reagents, there are side-reactions, and chief among these is the coupling reaction to give R·R compounds.[1] The extent of this coupling reaction varies between extreme limits,[2] and until recently it was essentially impossible, for example, to prepare allylmagnesium bromide because of the unusually high yield of diallyl.[3]

Perhaps the most unusual preparation of this type is that of benzohydrylmagnesium chloride, $(C_6H_5)_2CHMgCl$. Under ordinary conditions the yield of coupling product, *sym.*-tetraphenylethane, is astonishingly high and has reached 95.5%.[4] For this reason, the application of this RMgX compound in synthesis has followed the procedure of Barbier. This involves the preparation of the benzohydrylmagnesium halide in the presence of the reactant.[5] Ordinarily this procedure has two serious disadvantages:

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[1] Gilman and Fothergill, THIS JOURNAL, 50, 3334 (1928).

[2] See Giman, Zoellner and Dickey, *ibid.*, 51, 1576 (1929), for the yields of some RMgX compounds. Some typical RMgX compounds like phenylmagnesium bromide and *n*-butylmagnesium bromide can be prepared in essentially quantitative yields when an excess of magnesium is used.

[3] It is now possible to prepare allylmagnesium bromide in yields greater than 93%. See Giman and McGlumphy, Bull. *soc. chim.*, 43, 1322 (1928).

[4] Gilman and Kirby, THIS JOURNAL, 48, 1733 (1926).

[5] Gomberg and Cone, *Ber.*, 39, 1461 (1906); Bert, *Compt.* rend., 177, 324 (1923); Grignard and Ono, Bull. *soc. chim.*, 39, 830, 1589 (1926); Gilman and Kirby, THIS JOURNAL, 48, 1733 (1926); Levy and Lagrave, *Bull. soc.* chim., 43, 437 (1928).

first, the yields are low; second, the formation of the Grignard reagent may be retarded and, in some cases, actually inhibited.'"

We needed benzohydrylmagnesium chloride in connection with the extension of studies on the so-called abnormal reactions of Grignard reagents having α,β-unsaturation.[6] As a result of the present study, it is now possible to prepare this RMgX compound independently (and not in accordance with the Barbier procedure) and the yields are satisfactory (70%). Excellent yields of the corresponding carboxylic acid, diphenylacetic acid, have been realized by the customary procedure of carbonation.

Perhaps of greater significance than the development of a method for the preparation of this unusual Grignard reagent in satisfactory yields, is the direct observation of what appear to be transiently formed free radicals. During the addition of the benzohydryl chloride in ether to magnesium in ether, it was noted that a reddish color formed where the chloride came in contact with the ether containing magnesium and Grignard reagent. The same phenomenon was observed when the benzohydryl chloride was added to an ether solution of benzohydrylmagnesium chloride free of magnesium. With the rapid addition of halide to the Grignard solution, it was possible (in small containers) to have the color throughout the solution. The color disappears very shortly after its formation, and it is impossible to get the color when the Grignard reagent is used up.

It has already been suggested by Gomberg and Bachmann[7] that free radicals are formed initially in the *preparation* of Grignard reagents when iodine is used as a catalyst, as follows

$$\mathrm{Mg} + \mathrm{I_2} \longrightarrow \mathrm{MgI_2} \qquad (1)$$
$$\mathrm{MgI_2} + \mathrm{Mg} \longrightarrow 2\,\text{—MgI} \qquad (2)$$
$$\mathrm{RX} + \text{—MgI} \longrightarrow \mathrm{R}\text{—} + \mathrm{XMgI} \qquad (3)$$
$$\mathrm{XMgI} + \mathrm{Mg} \longrightarrow \text{—MgI} + \text{—MgX} \qquad (4)$$
$$\mathrm{R}\text{—} + \text{—MgX} \longrightarrow \mathrm{RMgX} \qquad (5)$$

In the absence of a catalyst, like iodine, it has been suggested[7] that the first step in the reaction is

$$2\mathrm{RX} + \mathrm{Mg} \longrightarrow \mathrm{R{\cdot}R} + \mathrm{MgX_2} \qquad (6)$$

and that the $\mathrm{MgX_2}$ so formed then reacts with magnesium in accordance with Reaction 1 to give —MgX which subsequently combines with the free radical to give the RMgX compound. However, we[1] are of the opinion that the formation of free radicals is the *first* step in the preparation of the Grignard reagent, even in the absence of any catalyst

$$2\mathrm{RX} + \mathrm{Mg} \longrightarrow 2\mathrm{R}\text{—} + \mathrm{MgX_2} \qquad (7)$$

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[6] Gilman and Kirby, THIS JOURNAL, 51, 3475 (1929); Gilman and Jones, *ibid.*, 51, 2840 (1929).

[7] Gomberg and Bachmann, *ibid.*, 49, 236 (1927). This article contains leading references to explanations for the catalytic influence of some reagents for initiating the preparation of organomagnesium halides.

and that then the MgX_2 reacts with magnesium (Reaction 2) to give the —MgX, which subsequently combines with the free radical (Reaction 5). Possibly both reactions occur.

Whatever may be the correct explanation, and both mechanisms as well as others may be correct, there is experimental evidence by Gilman and Fothergill[1] and Gilman and Kirby[8] in support of the intermediate formation of free radicals incidental to the preparation of Grignard reagents.

The transitory color observed on the addition of benzohydryl chloride to benzohydrylmagnesium chloride indicates that free radicals are also formed ***subsequent*** to the preparation of RMgX compounds. The free radicals so formed might account in part at least for the side reactions of coupling and disproportionation described by Gilman and Fothergill.[1]

$$(C_6H_5)_2CHMgCl + (C_6H_5)_2CHCl \longrightarrow 2(C_6H_5)_2CH— + MgCl_2 \qquad (8)$$

$$2(C_6H_5)_2CH— \longrightarrow (C_6H_5)_2CHCH(C_6H_5)_2 \qquad (9)$$

and, where disproportionation can occur, the following general reaction[1] might be written

$$2R— \longrightarrow R(+H) + R(—H) \qquad (10)$$

It is interesting to note that apparently the same color phenomena are observed on the addition of benzohydryl chloride to some RMgX compounds other than benzohydrylmagnesium chloride. This is not entirely unexpected in view of the studies by Fuson,[9] who showed that the coupling reaction is best interpreted under certain conditions, as follows

$$2RX + 2R'MgX \longrightarrow R{\cdot}R + R'{\cdot}R' + 2MgX_2 \qquad (11)$$

In accordance with this reaction it is readily understandable that the formation of R·R compound from the RX compound might have taken place as indicated in Reaction 9, written above. Actually, Späth[10] has suggested such a general mechanism, but this is the first case where we have observed the apparent intermediate formation of free radicals other than those of *tri*-arylmethyls[11] and related compounds. It should be possible to capture[12] these radicals and extend our knowledge of free radicals to new types.

[8] Gilman and Kirby, THIS JOURNAL, 51, 1571 (1929). Another interpretation does not involve —MgX, and consists in the direct union of $2R— + Mg \longrightarrow R_2Mg$. See Gilman and Brown, ibid., 52, November, 1930.

[9] Fuson, *ibid.*, 48, 830, 2681, 2937 (1926). These papers have an excellent review of earlier studies on the coupling reaction.

[10] Spath, *Monatsh.*, 34, 1965 (1913).

[11] See, Gilman and Zoellner, THIS JOURNAL, 51, 3493 (1929), for the preparation of triphenylmethylmagnesium chloride.

[12] See, Gilman and Fothergill, *ibid.*, 51, 3149 (1929), for studies on the capture of free radicals formed in the preparation and reactions of Grignard reagents.

After the manuscript was submitted for publication, it was found that benzohydrylmagnesium chloride reacted with benzophenone to give benzopinacol and tetraphenylethylene. This is evidence for the dissociation of this RMgCl compound. and for the disproportionation of benzohydryl radicals.

Experimental Part

The benzohydryl chloride used in these studies may not have been as pure as that prepared previously by Gilman and Kirby.[4] Two fractions were used. One of them boiled at 147–148° (6 mm.) (m. p. 9–11"), and the other at 148–150° *(6* mm.) (m. p. 13–15") The apparatus and method of analysis were those described by Gilman, Zoellner and Dickey.[2] However, the procedure had the following slight variations: ten drops of halide were used to initiate the reaction; heat was applied by means of a microburner under a wire gauze; as soon as reaction set in (two to three minutes), stirring was commenced; then, refluxing and stirring were continued for ten minutes prior to addition of the remaining halide in ether. There was no difficulty in starting the reaction when the customary small quantity (0.03–0.05 g.) of iodine was used as a catalyst.

Without going into details of a series of experiments, it may be stated at once that the yield is markedly affected by the quantity of fine magnesium (30–80-mesh). In an experiment using 5.07 g. (0.025 mole) of benzohydryl chloride, 6.1 g. (0.25 atom) of magnesium and a total of 74 cc. (0.74 mole) of ether, the yield was 51%. The time of addition of the halide was one hour, and with a two-hour period of addition the yield was 53%. It was noted that the formation of precipitate was slightly progressive. In contrast with this, the precipitation is more pronounced at the beginning of the preparation of *tert.*-butyl- and *tert.*-amylmagnesium chlorides,[13] and in these cases the precipitate (under optimal conditions) disappears when the preparation is about one-half completed.

When the ratio of magnesium and ether to the chloride was doubled, so that for each mole equivalent of benzohydryl chloride 20 atom equivalents of magnesium and 60 mole equivalents of ether were used, the yield was 57%. Here there was less precipitate and its formation was not progressive.

When 30 atom equivalents (9.12 g.) of magnesium and 60 equivalents (74 cc.) of ether were used with one mole equivalent (2.53 g.) of benzohydryl chloride boiling at 148–150° (6 mm.), and when the time of addition was one and one-half hours, the yield was 71%. In a like experiment with the halide boiling at 147–148° (6 mm.), the yield was 68%. In these experiments the smallest quantity of precipitate formed. It appears altogether reasonable that with a still higher ratio of magnesium, pure halide and slow addition, the yield can be significantly increased.

A larger-sized run was made in order to prepare the corresponding carboxylic acid. In this experiment the conditions were those described for the 51% yield preparation: 10.14 g. (0.05 mole) of the chloride was used and the time of addition was two hours. The yield by titration was 50%. After cooling the RMgCl solution to −15°, carbon dioxide was added[14] rapidly and was taken up almost instantly. The yield of diphenylacetic acid, $(C_6H_5)_2CHCOOH$, was 84% (based on the quantity of available RMgCl compound).[15] The identity of the acid was confirmed by a mixed melting point determination with an authentic specimen. In addition to the acid, there was isolated 2.5 g or 30% of *sym*-tetraphenylethane.

Summary

Under ordinary conditions it is practically impossible to prepare benzohydrylmagnesium chloride, $(C_6H_5)_2CHMgCl$, because of an extreme tend-

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'' Gilman and Zoellner, *Rec. trav. chim.*, 47, 1058 (1928).

[14] Gilman and Parker, THIS JOURNAL, 46, 2816 (1924).

[15] This high yield is remindful of the very high yield of triphenylacetic acid obtained by the carbonation of triphenylmethylmagnesium chloride.''

ency for coupling which results in a 95% yield of R·R compound. Directions are now available for the preparation of this unusual Grignard reagent in yields upwards of 70%. The coupling reaction is apparently due to the prior formation of free benzohydryl radicals, which are of red color and of short life.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MIDDLEBURY COLLEGE]

ALIPHATIC ACYLOINS. I. PREPARATION[1]

BY B. B. CORSON, W. L. BENSON AND T. T. GOODWIN

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The most promising method which has been described for the preparation of aliphatic acyloins involves the action of sodium on ethereal or benzene solutions of aliphatic esters. This reaction was first described by Bouveault and Locquin[2] and the following mechanism was assumed

$$\begin{gathered}2\mathrm{RCOOR'} + 4\mathrm{Na} \longrightarrow 2\mathrm{NaOR'} + \mathrm{RC(ONa){=}C(ONa)R}\\ \mathrm{RC(ONa){=}C(ONa)R} + 2\mathrm{H_2O} \longrightarrow \mathrm{RC(OH){=}C(OH)R} + 2\mathrm{NaOH}\\ \mathrm{RC(OH){=}C(OH)R} \longrightarrow \mathrm{RCHOHCOR}\end{gathered}$$

Other mechanisms have been suggested.[3]

According to the original directions the reaction was run at 0° except in one case, pivaloin (2,2,5,5-tetramethylhexanol-3-one-4), where the reaction temperature was that of the room. The implication was that the acetoacetic ester condensation would result at higher temperatures and it was suggested that acyloins represented an intermediate step in the acetoacetic ester condensation.[4] Other investigators, however, have used higher temperatures, with equally good results.[5]

When the original directions are followed the reaction proceeds very slowly. In preparing pivaloin at room temperature Bouveault found it necessary to allow the reaction mixture to stand for eight to ten days. The use of a higher reaction temperature cuts down the time from days to hours. It has been suggested that the slowness of reaction in this particular case was due to the highly branched chain and the absence of enolizable hydrogen in the starting material, ethyl trimethylacetate.[5a] However, following the original directions the reaction also goes very slowly

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[1] Preliminary work was done by N. E. Sanborn and P. B. Smith in 1928–1929.

[2] Bouveault and Locquin, *Bull. soc. chim.*, [3] 35, 629–643 (1906); *cf.* Bacon, *Am. Chem. J.*, 33, 68 (1905), and Higley, *ibid.*, 37, 293 (1907).

[3] (a) Scheibler and Voss, *Ber.*, 53, 388 (1920); (b) Scheibler and Emden, *Ann.*, 434, 265 (1923); (c) Egorova, *J. Russ. Phys.-Chem. Soc.*, 60, 1199 (1928); *C. A.*, 23, 2935 (1929); (d) *cf.* Gomberg and Bachmann, THIS JOURNAL, 50, 2762 (1928).

[4] Bouveault and Locquin, *Ann. chim. phys.*, [8] 19, 186 (1910).

[5] (a) Scheibler and Emden, *Ann.*, 434, 265 (1923); (b) Feigl, *Ber.*, 58, 2299 (1925); (c) *cf.* McElvain, THIS JOURNAL, 51, 3124 (1929).

with straight chain esters such as ethyl butyrate, We have not applied the modified directions to the preparation of pivaloin but we have prepared a very similar substance, 3,3,6,6-tetramethyl-octanol-4-one-5 from ethyl dimethylethylacetate and, as far as we could see, the reaction proceeded as smoothly with the latter as with simpler esters. In the course of this work we have prepared propionoin, the two isomeric butyroins, two valeroins and four capronoins at the reflux temperature of the ether solutions.

For solvent, Bouveault used either dry ether or dry benzene, but from our experience, ether is much superior to benzene. Scheibler[3a] found the same to be true in a similar reaction, the preparation of ester enolates from aliphatic esters.

The yield of once-distilled product (25° boiling point range) is around 50% of the theoretical amount. The yield of pure product (1–3° boiling point range) is considerably smaller owing to the necessity of repeated vacuum fractionation. At least two substances are always obtained, the acyloin proper and a higher-boiling liquid of approximately twice the molecular weight and of unknown structure. Certainiy, part of this second substance is formed during distillation and according to Bouveault the elevated temperature of distillation is responsible for all of it. A subsequent paper from this Laboratory will deal with this high-boiling by-product.

Also, a third substance is usually present, the 1,2-diketone (RCOCOR) corresponding to the acyloin (RCHOHCOR). Presumably autoxidation of the enediolate, $RC(ONa){=}C(ONa)R$,[5a] accounts for the presence of the diketone, although some mechanisms of acyloin formation envisage the diketone as an intermediate step. The greater part of the diketone can be removed from the once-distilled product by shaking with saturated sodium bisulfite but the last traces must be removed by distillation. Since the diketones are deep yellow and the acyloins pale yellow, the depth of color in the distilling column is a useful guide as to the progress of fractionation.

It is our experience that acyloins as obtained by distillation are always slightly yellow. Butyroin was fractionated in a vacuum six times in succession in the attempt to obtain a colorless product. The film of liquid flowing down the column appeared to be colorless but the butyroin which collected in the receiver had a tinge of yellow. Although it seemed impossible to remove the last traces of yellow by distillation, we finally discovered that exposure to sunlight quickly brought about that result. Usually, a one-hour exposure was sufficient. In only one case, that of a sample of isobutyroin made from ethyl isobutyrate, were we unable to remove the color; on the other hand, a sample of isobutyroin made from isobutyl isobutyrate decolorized easily. When these colorless acyloins are kept in the dark or in diffused light, the yellow color returns in several days. This color change can be repeated several times by alternately exposing to sunlight and keeping in the dark.

Scheibler[3b] has recorded the extreme light sensitivity of an aromatic substituted aliphatic diketone, tetrabenzyldiacetyl, the photo-reaction being to some extent reversible.

$$(C_6H_5CH_2)_2CHCOCOCH(CH_2C_6H_5)_2 \rightleftharpoons (C_6H_5CH_2)_2CHCHOHCOCH(CH_2C_6H_5)_2$$

It has long been known that aromatic 1,2-diketones are light sensitive and the best known example of this reaction is the conversion of yellow benzil into colorless benzil-benzoin.

It may be that the yellow color of aliphatic acyloins is due to a small amount of the corresponding yellow diketone and by analogy with Scheibler's findings it may be that the reversible color change is due to the reversible reduction–oxidation of the diketone–hydroxyketone system. Further work is now in progress in this Laboratory on the photochemical decomposition products of aliphatic acyloins.

For some time we did not realize that this color change was indicative of alteration in composition, since the refractive index and the density were identical in colored and colorless samples. Finally, it was discovered that the colorless samples had a considerably different carbon–hydrogen composition. Up to this time exposure of the acyloins to light had never Seen avoided, with the result that after a few weeks in the laboratory the acyloins were far from pure. After this discovery all the acyloins were redistilled and a low-boiling fore-run was found in every case. There was very little, if any, high-boiling residue. With these acyloins, refractive index and density are merely rough criteria of purity, e. g., a sample of n-valeroin which had been exposed to light still had the identical refractive index and density within 2 parts per 1000 although its carbon and hydrogen percentages had fallen 1.2 and 1.1%, respectively.

In the preparation of acyloins it is advisable to start with the methyl or ethyl ester of the acid in question. Although the reaction proceeds at least as fast and possibly faster[3"] with the higher esters such as iso-amyl, etc., it is difficult to obtain a pure product, due to contamination by the resulting high-boiling alcohol.

About 10% of the sodium becomes so thickly encrusted with sodium derivative that it is unable to react. Following these modified directions, satisfactory yields of acyloins are obtained with esters of acids from propionic up through caproic, but the limit has been reached in an acid of twelve carbons. With ethyl laurate and ethyl myristate only 20–30% of the sodium reacted in ten hours of heating followed by thirty-six hours of standing. The reaction was so incomplete that no attempt was made to isolate the products. Very likely potassium would extend the limits of the reaction. Acetoin cannot be prepared successfully by this method, due partly to its solubility in water and partly to its extreme sensitivity to alkali.

Aromatic acyloins have recently been prepared by Gomberg[3d] from both esters and acids by means of magnesious halide. With sodium, the free acid does not result in acyloin, the only product being the sodium salt of the acid. It may be that, under suitable conditions, the reaction would proceed, but at any rate, mere substitution of free acid for ester in the following directions results only in the sodium salt of the acid.

Experimental Part

General Procedure.—In a three-necked 2-liter round-bottomed flask were placed 1000 cc. of dry ether and 92 g. of sodium cut into small slices. We did not find it practicable to convert such large quantities of sodium into wire; thin slices were found quite suitable. First, the sodium was cut into sticks 10–13 cm. long and about 2.5 sq. cm. in cross section and stored in wide-mouthed, rubber-stoppered bottles. Just before using, the sodium was freed from oxide, weighed and cut under dry ether with a thin knife, into 5-mm. slices (thinner if possible). The middle neck of the flask was fitted with a mechanical stirrer (propeller type) and mercury seal combination. In one of the side necks was placed a reflux condenser and in the other a 125-cc. dropping funnel. The stirrer was started and the ether heated to the reflux temperature by means of a jet of steam impinging on the bottom of the flask. A pan was placed under the flask to catch the drip. The heating necessary to keep the ether refluxing varied with the ester used—with ethyl *n*-caproate and ethyl propionate considerable steam heating was required, whereas with iso-amyl isovalerate and isobutyl isobutyrate very little heating was required. Two-gram molecules of the ester in question was added at the rate of two drops per second to the stirred, hot mixture. Addition required two hours. The mixture was then stirred and steam-heated for an additional hour. A yellowish (occasionally reddish to light brown) solid began to appear in fifteen to thirty minutes and gradually increased in amount until practically all of the sodium had been converted into it and the contents of the flask was a thick mush. With ethyl butyrate 1000 cc. of ether was sufficient but with ethyl valerate and iso-amyl isovalerate it was necessary to introduce another 500 cc. of ether after half the ester had been added in order to keep the mixture sufficiently liquid to stir.

After standing for twenty-four hours the sodium salt was ready to be decomposed. Longer standing does no harm. If the mixture is to be allowed to stand for several days, the flask should be stoppered to prevent evaporation of ether and also to exclude air. The reaction mixture was poured (small amount at a time) into a 2-liter battery jar containing about 8 cm. of water full of cracked ice and layered with 5 cm. of ordinary ether. Each portion was brought into solution by stirring with a rod before another addition; excess of ice was maintained throughout the process. Pieces of unreacted sodium were removed with a wire skimmer, rinsed in a small dish of ether and finally dropped into a beaker of alcohol. Sometimes the mixture was fluid and poured nicely; sometimes it was thick and had to be removed by means of a long spatula. The layer of ether prevents the sodium from igniting; most of the sodium pops up and down at the ether–water interface. Although this decomposition is surprisingly free from fire hazard it is advisable to have wet towels and fire extinguishers handy.

In several runs toluene was substituted for ether. The reaction proceeded nicely in the boiling toluene but it was impossible to work up the product in the usual manner by pouring into water without frequent fires. Possibly the excess sodium could have been decomposed with alcohol or acetic acid.

After the sodium salt had been added and both the water and ether had become clear, the ether was separated. The water layer was extracted with two 250-cc. portions of ether and then discarded. The discarded water contains about 6 g. of organic acid as sodium salt. In the preparation of butyroin the greater part of this acid was butyric but there was a certain amount of a higher-boiling liquid which seemed to be dipropylglycolic acid. The combined ether was washed twice with strong sodium chloride solution. The ether was then distilled through a 30-cm. column until the residue was about 250 cc., the temperature at the top of the column being 42–44°. The ether should be distilled rapidly with a free flame since prolonged heating increases the yield of the high-boiling product at the expense of the acyloin. The residue was distilled in a vacuum and collected over a wide range, the object being to remove ether. The distillate was thoroughly shaken (occasionally over a period of one hour) with 100 cc. of saturated bisulfite solution to remove diketone. In most cases a solid separated, necessitating suction filtration. Finally, the product was redistilled in a vacuum, the yield being about 50% of the theoretical amount.

TABLE I

ANALYTICAL DATA

Freshly distilled acyloin[a]	Wt. taken, mg.	CO_2, mg.	H_2O, mg.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Propionoin[b]	26.38	60.75	23.79	62.02	62.81	10.42	10.09
$C_6H_{12}O_2$	23.41	54.06	21.39		62.98		10.22
	27.67	63.92	26.16		62.99		10.58
n-Butyroin[c]	20.55	50.22	20.52	66.61	66.63	11.18	11.17
$C_8H_{16}O_2$	18.54	45.45	18.39		66.86		11.10
Isobutyroin[d]	24.44	59.43	24.36	66.61	66.32	11.18	11.16
$C_8H_{16}O_2$							
n-Valeroin[e]	21.75	55.76	23.04	69.70	69.92	11.71	11.85
$C_{10}H_{20}O_2$	22.43	57.68	23.39		70.13		11.67
Isovaleroin[f]	19.98	51.39	20.86	69.70	70.13	11.71	11.68
$C_{10}H_{20}O_2$	16.26	41.70	16.58		69.93		11.41
n-Capronoin[g]	19.97	52.95	21.75	71.93	72.30	12.08	12.18
$C_{12}H_{24}O_2$	18.25	48.38	19.07		72.28		11.69
	17.90	47.66	19.09		72.59		11.93
Isocapronoin	21.66	57.13	23.35	71.93	71.92	12.08	12.06
$C_{12}H_{24}O_2$							
3,8-Dimethyldecanol-5-one-6, $C_{12}H_{24}O_2$	19.49	51.33	20.70	71.93	71.83	12.08	11.88
3,3,6,6-Tetramethyloctanol-4-one-5, $C_{12}H_{24}O_2$	18.81	49.70	19.86	71.93	72.06	12.08	11.81

[a] The ethyl butyrate used in the preparation of n-butyroin was kindly furnished by the Waukegan Chemical Co. The ethyl esters of isobutyric, *n*-valeric, isovaleric, n-caproic, isocaproic and β-methylvaleric acids were obtained by the oxidation of the corresponding primary alcohols [Robertson, "Organic Syntheses," John Wiley and Sons, Inc., New York, *1925*, Vol. V, *p.* 23]. The resulting esters (isobutyl isobutyrate, n-amyl n-valerate, etc.) were saponified. The free acids were liberated, purified by distillation and finally esterified with ethyl alcohol. The ethyl ester of dimethylethylacetic acid was prepared from *tert.*-amyl magnesium chloride plus carbon dioxide [Corson, Thomas and Waugh, THIS JOURNAL, 51, 1950 (1929)]. The amyl alcohols used in the synthesis of the four caproic acids were generously furnished by the Sharples Solvent Co. [b] Anderlini, *Gazz.* chim. *ital.*, 25, II, 51, 128 (1895). [c] Schmitz, *Ber.*, 24, 1273 (1891). [d] Basse and Klinger, *ibid.*, 31, 1218 (1898). [e] Basse and Klinger, *ibid.*, *31*, 1221 (1898). [f] Feigl, *ibid.*, 58, 2299 (1925). [g] Bouveault and Locquin, *Bull. soc. chim.*, [3] 35, 641 (1906).

TABLE II

PHYSICAL CONSTANTS

				$M_D(n^2)$		$M_D(n)$	
	B. p., °C. (corr.)	$n_D^{25.6}$		Calcd.	Pound	Calcd.	Found
Propionoin	50–53 (3 mm.)	1.4183	0.9310	31.26	31.39	51.8	52.1
n-Butyroin	80–82 (10 mm.)	1.4242	.9160	40.40	40.12	67.0	66.7
Isobutyroin	55–57 (3 mm.)	1.4159	.8990	40.40	40.16	67.0	66.6
n-Valeroin	90–92 (3 mm.)	1.4298	.9000	49.54	49.38	82.2	82.2
Isovaleroin	94–97 (12 mm.)	1.4260	.8930	49.54	49.32	82.2	82.0
a-Capronoin	105–107 (3 mm.)	1.4339	.8900	58.69	58.51	97.4	97.5
Isocapronoin	101–103 (3 mm.)	1.4326	.8865	58.69	58.60	97.4	97.6
3,8-Dimethyldecanol-5-one-6	102–104 (3 mm.)	1.4330	.8880	58.69	58.51	97.4	97.5
3,3,6,6-Tetramethyloctanol-4-one-5[a]	96–97 (3 mm.) (m. p., ±12°)	1.4471	.9300	58.69	57.58	97.4	96.2

[a] In this one case it should be noted that the actual molecular refraction did not check the theoretical. The carbon–hydrogen analysis, however, was satisfactory.

Carbon-hydrogen Analysis of Acyloins.—Aliphatic acyloins are difficult substances to burn properly. In order to obtain consistent analytical results the combustion must be slow and more oxygen than usual must be passed through the combustion tube. These substances are too volatile to be weighed in the usual combustion boat. Using Pregl's method of weighing the substance in small tubes containing a little potassium chlorate and ending in capillary tips, there were often small explosions during the combustion and finally one explosion was so violent that it wrecked the combustion tube. These explosions were due to the fact that the liquid did not vaporize from the tip but was forced out in drops by the pressure within. Finally, small ground-glass stoppered pyrex tubes (50 × 9 mm.) were used. These were ignited, cooled in a desiccator and weighed in a little wire frame which sat on the balance pan. The tube was then transferred to another wire frame and two drops of liquid were dropped into the tube from a small pipet. The tube was then half filled with previously ignited copper oxide powder, the ground-glass stopper was inserted and the tube was re-weighed. These tubes are easily handled by means of steel tweezers with curved tips.

Sodium Bisulfite Addition Product of Diketones.—Usually the amount of solid obtained on treatment of the crude acyloin with sodium bisulfite was small and was not further investigated. Bouveault removed diketone by means of bisulfite solution but he did not observe the formation of any solid product. Incidentally, we substantiated Bouveault's finding that ether interferes with the removal of diketone by means of bisulfite. With one run of isovaleroin which had stood for two weeks before it was worked up, bisulfite occasioned an appreciable warming and a considerable quantity of solid was obtained. The air-dried salt was analyzed and almost the theoretical figure was obtained for the sodium bisulfite addition product of the diketone. Later, the solids from n-capronoin and isobutyroin were analyzed and about twice the theoretical sodium percentage found; but there was this difference in procedure—the first salt was merely air-dried, whereas the last two were dried at 100° in a vacuum over concentrated sulfuric acid. The first analysis was therefore repeated on a sample which had been thoroughly dried, and the sodium percentage was then found to be about twice the theoretical. During the drying of the isovaleroin product considerable yellow oil came out of the solid and slowly evaporated into the sulfuric acid which was the drying agent. No oil was noticed in the drying of the other two salts.

Solid from Crude Isovaleroin.—*Anal.* Calcd. for $C_{10}H_{20}O_8Na_2S_2$: Na, 12.4. Found: Na, 12.8 (air-dried); 28.5 (dried at 100°).

Solid from Crude *n*-**Capronoin.**—*Anal.* Calcd. for $C_{12}H_{24}O_8S_2Na_2$: Na, 11.3. Found: Na, 24.4.

Solid from Crude **Isobutyroin.**—*Anal.* Calcd. for $C_8H_{16}O_8S_2Na_2$: Na, 13.1. Found: Na, 24.8.

These values are very close to that of sodium bisulfite (Na, 22.1) and sodium pyrosulfite (Na, 24.2). Possibly these addition products decompose at 100° into diketone and bisulfite.

Photochemical Decomposition.—Many analyses were made on acyloins which had been exposed to light for various lengths of time but in Table III are listed only those values which are farthest from the percentages of the original acyloins. The acyloins whose analyses are recorded below were exposed to sunlight for about two weeks. However, a much shorter exposure causes a decided change in the carbon and hydrogen percentages. This change seems to be least with the two capronoins, 3,8-dimethyl-decanol-5-one-6 and 3,3,6,6-tetramethyl-octanol-4-one-5. In every case the percentage of carbon and hydrogen dropped except with isocapronoin, where exposure to light resulted in raising the figures for both carbon and hydrogen.

TABLE III

ANALYTICAL DATA

Acyloin exposed to sunlight	Taken, mg.	CO_2, mg.	H_2O, mg.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Propionoin	21.66	46.63	18.13	62.02	58.71	10.42	9.36
n-Butyroin	22 07	49 75	19 73	66 61	81 48	11.18	10.00
Isobutyroin	18.43	43.33	17.53	66.61	64.12	11.18	10.64
n-Valeroin	21.20	53.14	20.14	69.70	68.36	11.71	10.63
Isovaleroin	17.65	44.59	17.45	69.70	68.90	11.71	11.06
n-Capronoin	22.34	56.58	22.35	71.93	69.07	12.08	11.19
Isocapronoin	18.60	49.48	20.60	71.93	72.55	12.08	12.39
3,8-Dimethyldecanol-5-one-6	17.43	45.83	17.17	71.93	71.70	12.08	11.03
3,3,6,6-Tetramethyl-octanol-4-one-5	22.49	58.62	23.43	71.93	71.09	12.08	11.66

Identification of **Butyroin.**—At first erratic analyses forced us to doubt that these substances were really acyloins. At this time we did not realize that aliphatic acyloins are difficult substances to burn and that they also undergo photochemical decomposition. Two derivatives of butyroin were prepared following Bouveault's directions.

Butyroin Acetate.—The boiling point was 113–115° (21 mm.), which is in agreement with Bouveault's figures, 117–118" at 21 mm.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.47; H, 9.75. Found: C, 65.06; H, 10.11.

Butyroin Osazone.—A good yield of yellow crystalline solid resulted. The compound melted at 140.5–141° (corr.), which agrees as well as can be expected with the uncorrected values given in the literature, 135°,[6] and 138°.[7]

Reaction between Sodium and *n*-**Valeric** Acid.—The reaction was carried out in the usual manner except that free acid was substituted for ester. A white solid quickly appeared which did not turn yellow or red as is the case when the reactant is ester. After standing for the usual length of time, a sample of this solid was removed, washed with dry ether, dried between filter paper and analyzed. The product was sodium valerate.

Anal. Calcd. for $C_5H_9O_2Na$: Na, 18.6. Found: Na, 16.9.

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[6] Klinger and Schmitz, Ber., 24, 1271 (1891).

[7] Basse and Klinger, ibid., 31, 1219 (1898).

When the run was worked up in the usual manner no valeroin was found. On the other hand, 50% of the valeric acid was recovered from the alkaline water layer.

Summary

Detailed directions are given for the preparation of aliphatic acyloins. Approximately 50% yields of the following acyloins were obtained: propionoin, n-butyroin, isobutyroin, *n*-valeroin, isovaleroin, *n*-capronoin, isocapronoin, 3,8-dimethyldecanol-5-one-6 and 3,3,6,6-tetramethyl-octanol-4-one-5. The last three substances are new.

Aliphatic acyloins easily undergo photochemical decomposition.

MIDDLEBURY, VERMONT

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XXX. THE COMPARATIVE HYDROLYSIS OF SOME DISACCHARIDES AND POLYSACCWARIDES

BY HAROLD HIBBERT AND EDMUND G. V. PERCIVAL[1]

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Introduction

The problem of the relative ease of hydrolysis of disaccharides and of polysaccharides such as starch and cellulose is an important one, not only from the scientific, but also from the industrial standpoint. Thus its solution is of great importance for a thorough understanding not only of the role played by starch as a "reserve material" in the vegetable kingdom but also of the close inter-relationship existing between starch and cellulose in plant metabolism. Also since it may be assumed that the structure of cellulose as a long chain of cellobiose units is now established on a reasonably firm basis, and that starch is presumably derived in a similar manner from maltose, the inter-relation of the reactions involving both analysis and synthesis of these products is of considerable interest.

It would also seem that a more intimate knowledge of the relative ease of hydrolysis of these products into glucose might throw some light on their relative stability and the bearing of the latter on the mode of linkage in the long-chain polysaccharides. Many of these hydrolytic changes, as shown in other researches to be published later, can be readily brought about under the influence of bacterial action as well as by the enzyme isolated from such organisms. There thus exists the possibility of co-relating two widely different types of hydrolytic agents.

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[1] Research Fellow, Pulp and Paper Research Institute, Montreal, Canada. The authors desire to express their thanks to the Canadian Pulp and Paper Association for financial assistance rendered in connection with this investigation.

Part I. Hydrolysis of Derivatives of Glucopyranose

The hydrolysis of starch by dilute acids has been investigated by Nanji and Beazeley,[2] Defren,[3] Meyer, Hopff and Mark[4] and others. Similarly Sherrard and Gauger,[5] Ost and Wilkening[6] and Simonsen[7] have studied the hydrolysis of cellulose by dilute acid. Since heat has to be applied, however, there is extensive decomposition of the glucose formed and the results are of no interest for comparing the two polysaccharides, the more so as cellulose is not dispersed in dilute acid.

Willstatter and Zechmeister[8] dissolved cotton cellulose in 41% hydrochloric acid and followed the course of the hydrolysis by observing the change in the specific rotation of the solution, and its reducing power. A discontinuity in the curve after about three hours was taken to indicate the presence of cellobiose. Sherrard and Froehlke[9] and Cunningham[10] employed a similar method, and Konig and Hühn[11] used a solution of zinc chloride in hydrochloric acid to disperse and hydrolyze cellulose.

Daish[12] investigated the hydrolysis of starch and maltose using fuming and concentrated hydrochloric acid, and he compared his results with those of Willstatter and Zechmeister.[8] Although his values indicate that starch hydrolyzes much more rapidly than cellulose, the fact that the experiments were not conducted under comparable conditions detracts from their value for purposes of comparison. Daish[12] indeed showed that maltose was hydrolyzed at about the same speed as starch itself, but as to how far the hydrolysis of cellulose is concerned with the breakdown of cellobiose was still left undecided. Freudenberg, Wolf, Knopf and Zaheer,[13] carrying out hydrolyses with *N* sulfuric acid at 70°, showed that cellobiose is much more difficult to break down than maltose. Willstatter and Zechmeister[8] had also called attention to the resistance towards hydrolysis of this disaccharide.

Selection of Reaction Medium

Instead of the inconvenient, fuming hydrochloric acid, it was decided to use zinc chloride, dissolved in hydrochloric acid, for the experiments on glucopyranose derivatives.

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[2] Nanji and Beazeley, *J. Soc. Chem. Ind.*, 215T (1926).

[3] "Eighth International Congress of Applied Chem.," 13, 113 (1912).

[4] Meyer, Hopff and Mark, Ber., 62, 1103 (1929).

[5] Sherrard and Gauger, *J. Ind. Eng. Chem.*, 15,1164 (1923).

[6] Ost and Wilkening, *Chem.-Ztg.*, 34, 461 (1916).

[7] Simonsen, *Z. angew. Chem.*, 11,219 (1898).

[8] Willstätter and Zechmeister, *Ber.*, 46,2401 (1913).

[9] Sherrard and Froehlke, THIS JOURNAL, 40, 173 (1918).

[10] Cunningham, *J. Chem. Soc.*, 113,173 (1918).

[11] Konig and Hühn, "Bestimmung der Zellulose in Holzarten," 1912, p. 55.

[12] Daish, J. *Chem. Soc.*, 105, 2053 (1914).

[13] Freudenberg, Wolf, Knopf and Zaheer, *Ber.*, 61,1743 (1928).

In the case of certain anhydrofructose compounds which were to be investigated, it was found advisable, owing to the rapidity of the hydrolysis and the decomposition of the fructose, to employ 0.1 N oxalic acid at 65°.

Preparation of Materials

Cellulose.—The material used was a pure absorbent cotton, having an a-cellulose value of 99.1%; ash, 0.05%, after drying at 60° (15 mm.).

β-Cellobiose.—This disaccharide was prepared from cellobiose octa-acetate (m. p. 227°), by the method of Maquenne and Goodwin,[14] as modified by Haworth and Hirst.[15] The product after purification had $[\alpha]^{20}_{D}$ 35°; m. p. 215°.

Cellodextrin (Cellobiosan) was prepared by Mr. J. G. Morazain, of this Laboratory, according to the method of Hess and Friese[16] (see also Meyer and Hopff);[17] $[\alpha]^{20}_{D}$ in 2 *N* NaOH, −4.1°.

Starch.—This was Kahlbaum's pure soluble starch for analysis, dried at 60° (15 mm.).

Inulin.—"Kiliani inulin" was "recrystallized" according to the method of Drew and Haworth[18] and dried at 60° (15 mm.).

Levan.—This was supplied by Mr. R. S. Tipson[19] of this Laboratory, and obtained by the action of *Bacillus mesentericus* on sucrose; after electrodialysis it was precipitated twice with alcohol; $[\alpha]^{20}_{D}$ −40°, dried at 60° (15 mm.).

The maltose, lactose, glucose, fructose, sucrose and galactose used in these experiments were authentic samples as shown by their physical constants, and were dried over phosphoric oxide in a vacuum.

The solvent, hereafter called (A), used in the experiments on the glucopyranose derivatives was a solution of anhydrous zinc chloride (1 part) in concentrated hydrochloric acid (d, 1.180) (2 parts) and was of d_4^{23} 1.464.

For the anhydrofructose derivatives 0.105 N oxalic acid (solution B) was used as the hydrolyzing agent.

The optical measurements were made with the Frič polarimeter recommended by the U. S. Bureau of Standards." All solutions were kept at 23 ± 0.1° by the use of a jacketed tube, except when oxalic acid was employed as hydrolyzing agent, in which case the temperature was 65 ± 0.2°.

Throughout these experiments *K* is calculated from the formula

$$K = \frac{1}{0.4343t} \log_{10} \cdot \frac{\alpha_\infty - \alpha_0}{\alpha_\infty - \alpha_t}$$

derived from the equation for *a* monomolecular reaction, in which *t* is time in seconds, α_0 is initial value of specific rotation (extrapolated), a, is final value of specific rotation and α_t is rotation at time *t*.

Experimental

For purposes of comparison it is necessary to have the cellulose completely dispersed prior to the hydrolysis and to carry out the experiments

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[14] Maquenne and Goodwin, Bull. *soc. chim.*, 31, 954 (1904).

[15] Haworth and Hirst, J. Chem. *Soc.*, 119, 193 (1921).

[16] Hess and Friese, *Ann.*, **450**, 40 (1926).

[17] Meyer and Hopff, *Ber.*, 63, 790 (1930).

[18] Drew and Haworth, J. *Chem. Soc.*, 133, 2690 (1928).

[19] Hibbert and Tipson, unpublished research. See preliminary note. THIS JOURNAL, 52, 2582 (1930).

[20] U. S. Bureau of Standards. Bulletin No. 44.

under identical conditions of temperature, because the velocity of a reaction is so markedly influenced by that factor.

The Hydrolysis of Cotton Cellulose at 23°.—About 0.25 g. of the dry material was weighed out accurately into a dry stoppered bottle, and 50 cc. of the solvent (A), at 23°, was added by means of a pipet. The mixture was shaken vigorously for five minutes and then carefully filtered through a weighed asbestos Gooch crucible, taking care to avoid loss of hydrogen chloride by employing the minimum amount of suction. The clear solution was transferred to the polarimeter tube and readings were taken at convenient times until the rotation became constant.

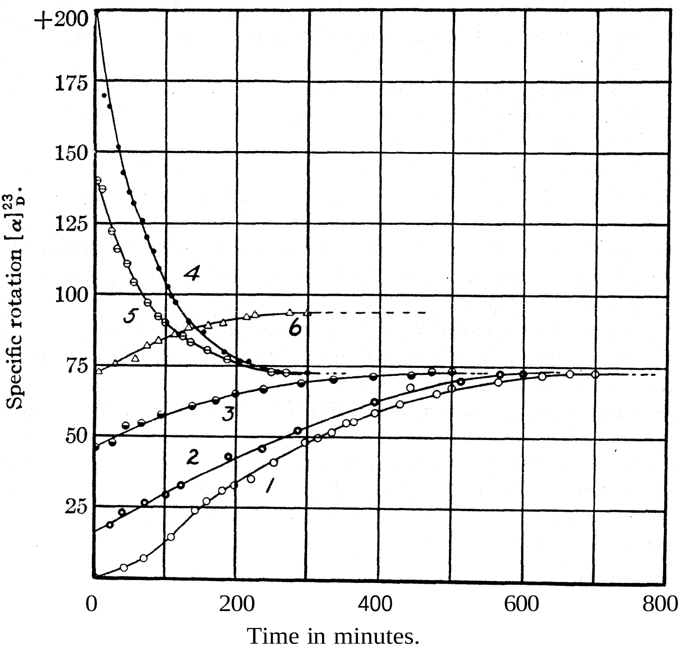

Fig. 1.—Rate of hydrolysis in zinc chloride–hydrochloric acid solution at 23°: 1, cellulose, ○; 2, cellodextrin O; 3, cellobiose, ◒; 4, starch, ●; 5, maltose, ⊖; 6, lactose, Δ.

The Gooch crucible was washed with distilled water and alcohol, dried at 105°, weighed and the increase in weight subtracted from the original weight of cellulose. This method was adopted because otherwise a slight cloudiness obscured the rotation. The amount of insoluble material after five minutes was usually about 7%. $[\alpha]^{23}_{D}$ was calculated on the basis of glucose, *i.* e., $[\alpha]^{23}_{D}$ observed X (162/180).

The rotation of anhydrous glucose in the same solvent (*A*) gave $[\alpha]^{23}_{D}$ +73.1 for $C = 1$.

The results are to be found in Table I and are plotted as Curve 1, Fig. 1.

The Hydrolysis of β-Cellobiose at 23°.—This disaccharide is completely soluble in solvent (A) to give a clear solution. The results are to be found in Table II and are plotted in Curve 3, Fig. 1.

TABLE I

THE HYDROLYSIS OF CELLULOSE AT 23°

Concentration, 0.454 g. of cellulose in 100 cc. of solvent (A)

Time, min.	$[\alpha]^{23}_{D}$	K X 10^4	Time, min.	$[\alpha]^{23}_{D}$	K X 10^4
0	0	...	335	51.5	0.61
42	+ 3.4	0.18	355	54.9	.66
75	6.9	.22	365	55.6	.66
105	14.4	.35	392	58.3	.69
156	24.0	.47	429	61.7	.73
160	27.4	.49	479	65.2	.79
182	30.9	.51	502	67.2	.83
199	32.9	.50	565	69.9	.96
223	35.0	.49	625	72.0	1.24
255	41.0	.54	665	72.7	...
298	48 0	.60	700	\$72.7	...
315	49.4	.60			

The reaction is thus shown not to be of the monomolecular type. Mean value of $K = 0.61 \times 10^{-4}$.

TABLE II

EXPERIMENTAL RESULTS

Concentration, 0.574 g. of cellobiose in 100 cc. of solvent (A)

Time, min.	$[\alpha]^{23}_{D}$	K × 10^4	Time, min.	$[\alpha]^{23}_{D}$	K × 104
0	+46.1	..	136	60.2	0.91
2	46.4	0.90	180	63.0	.93
10	46.5	.89	250	66.5	.95
16	48.7	1.05	296	68.7	1.02
21	49.9	1.20	339	69.3	0.96
37	52.1	1.13	388	70.5	1.00
61	54.4	1.10	449	71 6	1.07
94	56.3	0.95	508	73.1	..
113	59.0	.96	560	+73.1	..

Mean value of $K = 1.0 \times 10^{-4}$. The reaction is of the monomolecular type.

The Hydrolysis of Cellodextrin at 23°.—The results (Table III) indicate that the hydrolysis is not monomolecular, and that the polysaccharide occupies an intermediate position between cellulose on the one hand and cellobiose on the other. The values are plotted in Curve 2, Fig. 1.

TABLE III

EXPERIMENTAL RESULTS

Concentration, 0.550 g. of cellodextrin in 100 cc. of solvent (A)

Time, min.	$[\alpha]^{23}_{D}$	K X 10^4	Time, min.	$[\alpha]^{23}_{D}$	K X 10^4
0	\$16.5	..	238	46.0	0.52
12	18.4	0.48	287	52.2	.57
39	22.7	.50	394	62.6	.73
71	26.4	.46	443	67.5	.91
101	29.5	.44	513	69.9	.99
123	32.8	.46	573	72.5	..
190	43.0	.56	600	+72.5	..

The Hydrolysis of Starch at 23°.—Using the same technique, the hydrolysis of starch was investigated. The results are to be found in Table IV and are plotted on Curve 4, Fig. 1.

TABLE IV

EXPERIMENTAL RESULTS

Concentration, 0.448 g. of starch per 100 cc. of solution

Time, min.	$[\alpha]^{23}_D$	$K \times 10^4$	Time, min.	$[\alpha]^{23}_D$	$K \times 10^4$
0	+200.0	..	102	103.0	2.36
12	169.7	3.79	109	98.6	2.05
19	165.6	2.77	114	97.4	2.41
32	151.7	2.49	133	90.4	2.46
39	142.6	2.58	155	87.0	2.58
47	136.0	2.49	185	80.0	2.40
55	132.1	2.32	205	77.0	2.49
66	126.0	2.27	219	76.5	2.73
73	120.0	2.29	258	73.0	..
82	115.6	2.25	300	+73.0	..
90	109.2	2.33			

Mean value of $K = 2.45 \times 10^{-4}$. The reaction is apparently monomolecular after the first half hour.

The Hydrolysis of Maltose at 23°.—The results depicted in Table V and plotted in Curve 5, Fig. 1, indicate that the reaction is monomolecular.

TABLE V

EXPERIMENTAL RESULTS

Concentration, 0.552 g. of maltose in 100 cc. of (A)

Time, min.	$[\alpha]^{23}_D$	$K \times 10^4$	Time, min.	$[\alpha]^{23}_D$	$K \times 10^4$
0	+142.8	..	100	90.0	2.36
2	140.1	..	125	85.3	2.33
9	137.1	1.84	136	83.1	2.37
23	122.2	2.46	160	80.2	2.36
31	116.1	2.68	188	77.4	2.43
45	110.3	2.36	239	74.5	2.60
55	104.2	2.47	250	72.8	..
75	97.2	2.37	270	+72.8	..
90	92.3	2.44			

Mean $K = 2.40 \times 10^{-4}$.

TABLE VI

THE HYDROLYSIS OF LACTOSE AT 23°

Concentration, 1.560 g. of lactose in 100 cc. of solvent (A)

Time, min.	$[\alpha]^{23}_D$	$K \times 10^4$	Time, min.	$[\alpha]^{23}_D$	$K \times 10^4$
0	+72.4	..	133	87.7	2.49
4	72.8	..	161	88.8	2.78
28	73.0	..	182	89.9	2.67
56	76.9	2.80	216	92.0	2.57
73	81.7	2.90	247	92.8	2.83
90	83.4	2.63	275	93.5	..
113	85.4	2.43	300	+93.5	..

Mean value of $K = 2.84 \times 10^{-4}$. The reaction again is of the monomolecular type.

Since the results seemed to indicate that a β-biose is hydrolyzed much more slowly than an a-biose, it appeared of interest to determine whether lactose (which is a β-galactoside) hydrolyzes as slowly as cellobiose. The results are to be found in Table VI and are plotted in Curve 6, Fig. 1.

Discussion of Results

Table VII shows the mean values of the hydrolysis constant K for the substances indicated.

TABLE VII

VALUES OF THE HYDROLYSIS CONSTANT

Substance	Cellobiose	Starch	Maltose	Lactose
$K \times 10^4$	1.00	2.45	2.40	2.84

These experiments establish the fact that no generalization can be made as to the rate of hydrolysis of a disaccharide, and the mode of union of the building units with one another. This was also emphasized by Freudenberg, Wolf, Knopf and Zaheer,[13] who carried out the hydrolyses at 70° in N sulfuric acid solution for a large number of glucosides and disaccharides. These workers showed that under their experimental conditions, maltose (a-linkage) is hydrolyzed more than twice as rapidly as cellobiose (β-linkage) and that lactose (β-linkage) is hydrolyzed a little faster than maltose; this is confirmed by the present results.

The conclusions of Willstatter and Zechmeister[8] with regard to the discontinuity in their curve for the hydrolysis of cellulose are not confirmed in the present instance and it is suggested their results are possibly due to temperature variations. There would appear to be no theoretical significance whatever to the discontinuity as found by these authors. It would mean either that the hydrolysis had stopped, or that a substance of zero or negative rotation was being formed, whereas cellobiose was shown to have a positive equilibrium rotation value in their solvent. It is noteworthy that these authors in their determination of the reducing power found no such steps in the curve, and the same may be said of the results of Sherrard and Froehlke.[9]

The slow hydrolysis of cellulose is due to a great extent to the slow hydrolysis of cellobiose. The reaction is not monomolecular and the hydrolysis constants tend toward the value experimentally found for cellobiose under the same conditions.

If cellobiose is a reversion product as Hess[21] suggests, the time for the hydrolysis would be abnormally long because the following chain of reactions must, in this case, take place

$$\text{Cellulose} \longrightarrow \text{Glucose} \longrightarrow \text{Cellobiose} \longrightarrow \text{Glucose}$$

The fact that the cellobiosan of Hess and Friese[16] (which is regarded as a cellulosedextrin in the recent paper by Meyer and Hopff)[17] occupies an

[21] Hess, "Die Chemie der Zellulose," Leipzig, Germany, 1928, p. 494.

intermediate position between cellulose and cellobiose is further evidence against Hess' viewpoint.

The observations of Konig and Hühn, who found maxima in the case of the hydrolysis of different celluloses using solvent (A), are not confirmed except that it is apparent that the maxima they refer to are due to the destruction of glucose on standing, the solution becoming yellow and diminishing in $[\alpha]^t_D$ after thirty hours.

Willstatter and Zechmeister[8] considered that the amount of isomaltose formed in a 1% solution of glucose in fuming hydrochloric acid was negligible. This has been contested by Irvine and Soutar[22] but there seems to be little doubt that in the dilute solution used for these experiments (0.5%) the amount of isomaltose present at equilibrium would not affect the conclusions.

The difference in the rate of hydrolysis of starch and cellulose under identical conditions is shown to be due mainly to the difference in the rates of hydrolysis of the corresponding disaccharides, maltose and cellobiose, respectively. There would seem to be, therefore, no foundation for the belief that the glucose units in these polysaccharides possess a different ring system; the only difference between starch and cellulose, as far as hydrolysis is concerned, would seem to be due to the mode of linking of the glucose residues and the physical nature of the substances (see also Haworth[23] and Meyer, Hopff and Mark[4]).

It has been shown (Table III) that after the first half hour the hydrolysis of starch is practically monomolecular. Daish, using both concentrated and fuming hydrochloric acid, concluded that the hydrolysis of starch was not monomolecular but varied about 20% from that condition. He showed, however, that maltose did follow a monomolecular course and indicated that the two substances were hydrolyzed at almost the same rate. This is confirmed by the present series of observations.

The great influence of concentrated hydrochloric acid on the equilibrium rotation value was pointed out by Daish and has been observed repeatedly by other workers.

In the particular case of the zinc chloride–hydrochloric acid solvent (A) used, the equilibrium rotation between α- and β-glucose is shifted from +52.5 to +73.1°.

Part II

The Hydrolysis of Derivatives of Anhydrofructose.—It was of particular interest to determine the relation of levan to inulin. The former, as shown by Hibbert and Tipson,[19] consists of γ-fructose units linked together in the 2,6-positions. On the other hand, Haworth and Learner[24] provide con-

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[22] Irvine and Soutar, *J. Chem. Soc.*, 117, 1489 (1920).

[23] Haworth, "The Constitution of Sugars," London, 1929, pp. 83, *et seq.*

[24] Haworth and Learner, *J. Chem. Soc.*, 133, 619 (1928).

clusive evidence that inulin consists of fructofuranose units joined in the 1,2-positions.

Experiments on the comparative hydrolyses of these polysaccharides were carried out at 65 ± 0.2° using $N/10$ oxalic acid solution (B).

Experimental

The solutions were made up at 70° and rapidly transferred to the jacketed polarimeter tube. Corrections for the expansion of the glass, pipet and contained liquid were applied and all the results are calculated with the volumes reduced to 20°.

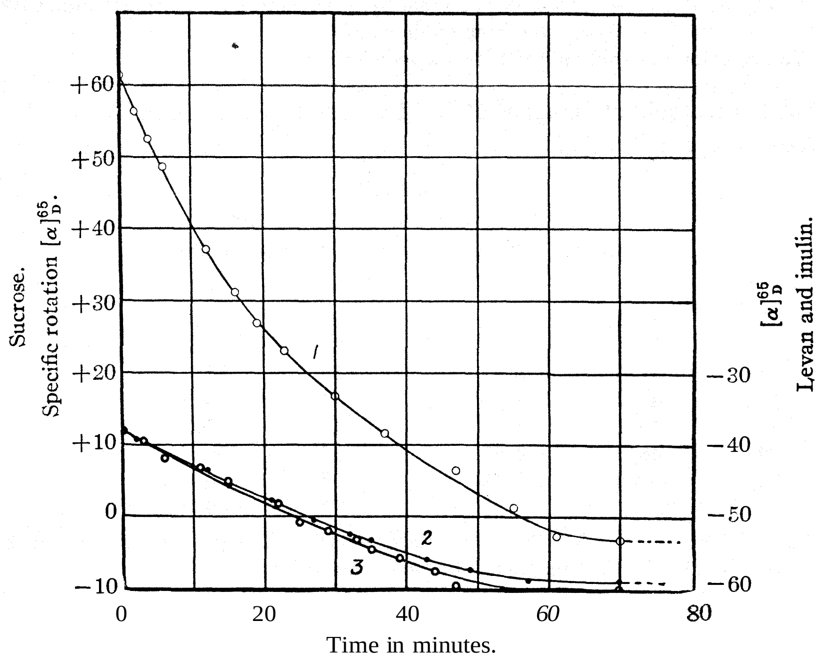

Fig. 2.—Rate of hydrolysis in N oxalic acid solution at 65°: *1*, sucrose, O; 2. inulin, ●; 3, levan, O.

The specific rotation of fructose at 65° may be calculated from the equation of Jungfleisch and Grimbert.[25]

$$[\alpha]^t_D = -[101.38 - 0.56t + 0.108(c - 10)]$$

where t is temperature in °C., and c is concentration in grams per 100 cc. Thus for a 1% solution at 65° $[\alpha]^{65}_D = -64.0$ in water; found, $[\alpha]^{65}_D$ −64.9 in solvent (B) for fructose.

The Hydrolysis of Inulin at 65°.—The results are given in Table VIII and plotted in Curve 2, Fig. 2.

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[25] Jungfleisch and Grimbert, *Compt. rend.*, *107*, 390 (1888).

TABLE VIII

THE HYDROLYSIS OF INULIN AT 65°

Concentration, 1.172 g. of inulin in 100 cc. of solvent (B)

Time, min.	$[\alpha]^{65}_D$	$K \times 10^4$	Time. min.	$[\alpha]^{65}_D$	$K \times 10^4$
0	-38.0	..	32	52.5	4.94
2	39.2	4.91	35	53.3	5.10
6	42.1	4.14	43	56.1	6.80
12	43.5	4.34	49	57.5	..
15	45.7	5.10	57	58.7	..
21	47.8	5.02	70	-58.7	..
27	50.5	4.75			

Mean value of $K = 5.01 \times 10^{-4}$. Final $[\alpha]^{25}_D = -80.0°$. Calcd. for inulin 100% fructose $= -85.2°$. % fructose from inulin = 94.0%.

The reaction does not appear to be monomolecular.

The Hydrolysis of Levan at 65°.—The results are given in Table IX and plotted in Curve 3, Fig. 2.

TABLE IX

THE HYDROLYSIS OF LEVAN AT 65°

Concentration, 1.227 g. of levan in 100 cc. of solvent (B)

Time, min.	$[\alpha]^{65}_D$	$K \times 10^4$	Time, min.	$[\alpha]^{65}_D$	$K \times 10^4$
0	-38.0	..	29	52.1	5.99
3	39.4	3.64	33	53.3	6.00
6	41.9	5.42	35	54.6	6.68
11	43.2	4.08	39	55.9	7.18
15	45.2	4.40	44	57.7	8.56
22	48.3	4.77	47	59.7	..
25	50.8	5.72	52	60.0	..
			70	-60.0	..

Mean value of $K = 5.66 \times 10^{-4}$. $[\alpha]^{26}_D$ $-83.0°$. Calcd., $-85.8°$. % fructose from levan = 96.7%. The reaction is not monomolecular.

The Inversion of Cane Sugar at 65°.—The results are given in Table X and plotted in Curve 1, Fig. 2.

TABLE X

THE INVERSION OF CANE SUGAR AT 65°

Concentration, 1.258 g. of sucrose in 100 cc. of solvent (B)

Time, min.	$[\alpha]^{65}_D$	$K \times 10^4$	Time. min.	$[\alpha]^{65}_D$	$K \times 10^4$
0	+61.5	..	23	23.1	6.62
2	56.4	5.49	30	16.6	6.71
4	52.5	6.30	37	11.5	6.81
6	48.7	6.19	47	6.4	6.95
12	37.1	6.65	55	+1.3	..
16	31.3	6.63	61	-2.6	..
19	26.9	6.80	70	-2.6	..

Mean value of $K = 6.50 \times 10^{-4}$. These figures indicate a monomolecular reaction.

Discussion of Results

It is to be noticed that inulin yields only 94% while levan yields 97% of its weight as fructose according to the values of the specific rotations.

This has been noted repeatedly in the case of inulin and is attributed to a difructose anhydride by Jackson and Goergen.[26]

It appears that the three anhydrofructose derivatives studied hydrolyze under the experimental conditions at about the same speed. This is illustrated in Table XI, showing the mean velocity constants.

TABLE XI

MEAN HYDROLYSIS CONSTANT AT 65°

Substance	Sucrose	Levan	Inulin
$K \times 10^4$	6.50	5.66	5.01

The constants in the case of levan and inulin (Tables IX and X) indicate that the process is not monomolecular, since the values of K, in general, rise. They are sufficiently close, however, to indicate that these two polysaccharides belong to the same group of substances.

Summary

1. The rates of hydrolysis of cellulose, cellobiose, cellodextrin, starch, maltose and lactose, in a zinc chloride–hydrochloric acid solution, are compared at 23°.
2. It is concluded that the slow hydrolysis of cellulose is, in a large part, due to the slow hydrolysis of cellobiose; that cellobiose is not a reversion product, and that there seem to be no grounds to suppose that starch and cellulose are essentially different, except for the a-linkages in the former and the 8-unions in the latter.
3. The rates of hydrolysis of sucrose, levan and inulin in 0.1 *N* oxalic acid solution at 65° have been measured.
4. It is established that these anhydrofructose derivatives hydrolyze at almost the same rate and it is concluded that this behavior is related to the γ-fructose residue present in each.
5. The technique developed is of possible application in the determination of the configurations of unknown polysaccharides.

MONTREAL, CANADA

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[26] Jackson and Goergen, U. S. *Bureau of Standards, Journ. Res.*, 3, 28 *(1929)*.

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

PIPERIDINE DERIVATIVES
X. THE PHENYLPIPERIDYLCARBINOLS

BY KENNETH E. CROOK AND S. M. McELVAIN

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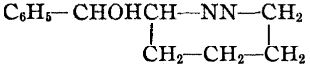
Since the publication[1] of the summarized work of Chen and others on the pharmacological properties of ephedrine, a number of papers have appeared in the chemical literature in which the preparation and properties of certain synthetic homologs of this important drug have been described.[2] These synthetic compounds in general have been of the type $ArCHOH\text{-}CHR_1NHR_2$, where Ar is a phenyl or alkyl substituted phenyl radical and R_1 and R_2 are various alkyl radicals. In certain cases R_1 is a phenylalkyl radical.

This paper describes the preparation and properties of the three phenylpiperidylcarbinols (I, II, III) as an effort to extend the synthetic ephedrine-like compounds to other types of structure. The relationship between the structure of these carbinols and ephedrine (IV) seemed interesting on account of the fact that the secondary amino group could be placed at different positions relative to the secondary alcohol group without increasing the carbon content of the molecule or altering materially the characteristic ephedrine-like structure.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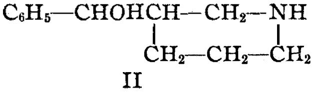
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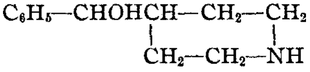
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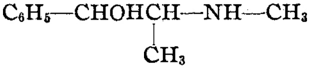
IV

The phenyl-2-, -3- and -4-piperidylcarbinols were obtained by the catalytic reduction of 2-, 3- and 4-benzoylpyridine hydrochlorides using Adams' platinum-oxide platinum black catalyst. The 2-benzoylpyridine was so weakly basic that due to the hydrolysis of its hydrochloride the catalyst was rendered inactive by the precipitation of the free base upon it. This difficulty was overcome by carrying out the reduction with an excess of hydrochloric acid in the solution. No similar difficulty was encountered in the reduction of the 3- and 4-benzoylpyridine hydrochlorides.

The reduction of 2-benzoylpyridine produced both diastereoisomeric racemic phenyl-2-piperidylcarbinols. One isomer (A) melted at 141–142°

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[1] Chen and Kao, *J. Am. Pharm. Assocn.*, 15, 625 (1926).

[2] Adams, Hyde and Browning, THIS JOURNAL, 50, 2287 (1928); Johnson and Manske, *ibid.*, 51, 1906 (1929); Fourneau and Barrelet, *C. A.*, 24, 352 (1930); de Buruaga, *C. A.* 24,596 (1930)

and the other (B) melted at 171–173°. Both isomers were isolated as the free bases and in the ratio of about three parts of A to one part of B. It was found that isomer A could be changed into isomer B to some extent by heating at 100° for forty-eight hours with 25% hydrochloric acid. The separation and purification of these racemic diastereoisomers are made possible by the fact that the hydrochloride of B is much more soluble in an alcohol-ether mixture than the hydrochloride of A, while the free base, B, is considerably less soluble than the free base A in water containing 4% alcohol. The details of the isolation and the conversion of the lower-melting into the higher-melting isomer are given in the experimental part of the paper. The amount of material that was available did not allow for any extended search to be made for the diastereoisomeric phenyl-3-piperidylcarbinols; consequently only one of these racemic mixtures was obtained. Obviously such isomerism would not be present in a structure such as phenyl-4-piperidylcarbinol.

The 2- and 4-benzoylpyridines were prepared by the oxidation of 2- and 4-benzylpyridines. 3-Benzoylpyridine was prepared from nicotinic acid by the method of LaForge.[3]

Pharmacological Properties.—The isomeric phenylpiperidyl carbinols are being studied pharmacologically by Messrs. Edward E. Swanson and Charles L. Rose of The Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana. They have reported that each of these carbinols has the same pharmacological properties as ephedrine, but is somewhat less active. The details of this pharmacological investigation will be published by them elsewhere.

Experimental

All melting points and boiling points herein given are corrected.

The 2- and 4-benzyl- and benzoylpyridines were prepared by a modification and, it is believed, an improvement of the methods which have been described by Tschitschibabin[4] and LaForge[3] for these compounds. Since specific directions were not found in the available literature, the procedures which proved most satisfactory are given below in considerable detail.

2-Benzylpyridine.—A mixture of 300 g. of benzyl chloride, 200 g. of dry pyridine and 3 g. of powdered copper was placed in a 2-liter flask fitted with a reflux water condenser and thermometer dipping into the contents of the flask. The mixture was slowly heated to 70°, after which the heat of the reaction caused the temperature to continue to rise to about 115°, when the liquid began to boil. At the first indication of boiling, the flask was surrounded by an ice-bath and cooled for three to five minutes until the violent reaction was over. The water condenser was then replaced by an air reflux condenser and the flask contents heated rapidly in an oil-bath to 225–230°, then slowly to 240–245°. A small amount of liquid distilling out of the top of the flask was discarded. The temperature was held at 240–245° for three hours, after which time the reaction

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[3] LaForge, THIS JOURNAL, 50, 2484 (1928).

[4] Tschitschibabin, *Chem. Centr.*, 72, II, 127 (1901); 73, I, 206 (1902); 87, II, 146

mixture was cooled to 75–100°, poured into 750 cc. of warm water which contained 50 cc. of concd. hydrochloric acid and chilled in an ice-bath. The black solution was poured off from a small amount of tar, made alkaline with sodium hydroxide, extracted with benzene, and the benzene solution dried over potassium hydroxide. After evaporation of the solvent, the material was distilled,' giving about 175 g. of crude benzylpyridines boiling between 260 and 310°, together with some higher-boiling material which was discarded. The 260–310° fraction was carefully fractionally distilled at atmospheric pressure through a 6-inch Vigreaux column sealed onto a flask. After three fractionations, the following fractions were obtained

279–282°	65–75 g.	285–288°	17–23 g.
282–285°	28–31 g.	288–299°	12–20 g.

The fractions boiling between 282 and 299" were used in the preparation of 4-benzoylpyridine (see below).

Fifty grams of the 279–282° fraction was added to a solution of 105 g. of picric acid in 3 liters of alcohol and refluxed for thirty minutes. The solution was then quickly cooled to about 32° in an ice-bath with stirring and the impure 2-benzylpyridine picrate which precipitated quickly filtered off. This crude picrate was dissolved in 3 liters of hot alcohol, cooled in an ice-bath with stirring to about 32" and again rapidly filtered. A second recrystallization from the same quantity of alcohol, but cooled to 20" before filtering, yielded 57–59 g. of pure 2-benzylpyridine picrate, m. p. 139.5–140.5°. If the relative amount of alcohol used in recrystallization was decreased or the solutions cooled to lower temperatures than indicated, additional recrystallizations were found to be necessary.

A suspension of 40 g. of 2-benzylpyridine picrate in about 1 liter of hot water was made strongly alkaline with ammonium hydroxide. The 2-benzylpyridine separated as an oil and, after cooling to 40°, was extracted with benzene. After drying over potash, the benzene was distilled off, leaving 16 g. of 2-benzylpyridine which boiled at 276.8–277.2° (737 mm.).

2-Benzoylpyridine.—Eighty-eight grams of 2-benzylpyridine was suspended in about 2 liters of water contained in a 3-necked flask fitted with reflux condenser, mechanical stirrer and thermometer which dipped below the surface of the liquid. To this suspension 115.5 g. of potassium permanganate was added in five or six portions. each portion being added only after the preceding ohe was practically decolorized. The temperature was held at 70° until after addition of the last portion of the oxidizing agent, and then raised to 100° until all the permanganate had reacted. After cooling, the liquid was layered over with benzene, stirred vigorously and the benzene solution of 2-benzoylpyridine drawn off, dried over potassium hydroxide and the solvent evaporated. The residue on distillation yielded 85–89.5 g. of 2-benzoylpyridine that boiled at 170–172° (10 mm.).[5]

This 2-benzoylpyridine gave a picrate from alcoholic solution that melted at 121–123°. After two recrystallizations from alcohol, the melting point of this picrate was 122–123°. Tschitschibabin[4] reports the melting point of this particular picrate as 130°. Further recrystallization, however, did not change the melting point. The purity of the compound obtained in the present work was checked by preparing some 2-benzoylpyridine from pure picolinic acid by the procedure described below for the preparation of 3-benzoylpyridine from nicotinic acid. The 2-benzoylpyridine so obtained gave a picrate which also melted at 122–123° and a mixture of the picrates prepared by the two methods melted at the same temperature.

2-Benzoylpyridine Hydrochloride.—When 2-benzoylpyridine was dissolved in

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[5] *Cf.* Wolffenstein and Hartwich, *Ber.*, 48,2043 (1915).

ether and dry hydrogen chloride passed in, a liquid hydrochloride separated that was difficult to crystallize. After solution in acetone and evaporation under diminished pressure to remove excess hydrochloric acid, the thick liquid was allowed to stand for three weeks, when about half had crystallized. One recrystallization from anhydrous acetone gave a white, crystalline hydrochloride, m. p. 126–128°.

Anal. Subs., 0.4567, 0.3917: AgCl, 0.2987, 0.2563. Calcd. for $C_{12}H_{10}ONCl$: Cl, 16.15 Found: Cl, 16.18, 16.19.

4-Benzoylpyridine.—The fractions of the benzylpyridine boiling between 282 and 299° were oxidized with potassium permanganate in a similar manner to that described above in the preparation of 2-benzoylpyridine. The crude 4-benzoylpyridine was added to a solution of double its weight of picric acid in sufficient alcohol to retain the picrate in solution at the boiling point. On cooling, nearly pure 4-benzoylpyridine picrate separated. One to two recrystallizations from the minimum quantity of boiling alcohol necessary for solution gave pure 4-benzoylpyridine picrate which melted at 159–160°. This picrate was decomposed as in the case of the 2-benzylpyridine picrate, yielding 4-benzoylpyridine, b. p. 313.5–314° (742 mm.), which solidified immediately to a white solid that melted without recrystallization, at 71.5–72.5°. In one run the three higher-boiling fractions of crude benzylpyridines were oxidized and purified separately, the yields of 4-benzoylpyridine being

75 g. of the 282–285° fraction gave 22.5 g. of 4-benzoylpyridine
38.5 g. of the 285–288° fraction gave 17.0 g. of 4-benzoylpyridine
31.5 g. of the 288–299° fraction gave 15.6 g. of 4-benzoylpyridine

In other runs the three fractions were combined before oxidation and there was obtained 32–33 g. of 4-benzoylpyridine for each 100 g. of material boiling between 282–299°.

4-Benzoylpyridine Hydrochloride.—Dry hydrogen chloride was passed into a solution of 10 g. of 4-benzoylpyridine in 250 cc. ether. The white, crystalline hydrochloride was recrystallized once from alcohol–ether, yielding 10 g. of the hydrochloride, m. p. 195–197°.

Anal. Subs., 0.6494, 0.7821: . AgCl, 0.3575, 0.5097. Calcd. for $C_{12}H_{10}ONCl$: Cl, 16.15. Found: Cl, 16.10, 16.12.

3-Benzoylpyridine was made by the method given by LaForge.[3] The only variation from his procedure was that the 3-benzoylpyridine was purified as the hydrochloride instead of as the picrate. The purified hydrochloride melted at 160–162°.

Anal. Subs., 0.3581, 0.4013: AgCl, 0.2321, 0.2598. Calcd. far $C_{12}H_{10}ONCl$: Cl, 16.15. Found: Cl, 16.03, 16.01.

Phenyl-2-piperidylcarbinol.—The 2-benzoylpyridine is very weakly basic and a solution of its hydrochloride in water appears cloudy due to hydrolysis. On attempting to reduce a solution of the hydrochloride in water with platinum-oxide platinum black catalyst which had previously been reduced in water, the eatalyst collected in small clumps and no hydrogen was absorbed. The addition of a 75% excess of hydrochloric acid would usually cause the catalyst to whip up into suspension and reduction then proceeded normally. To determine the optimum conditions for reduction in hydrochloric acid solution, the following experiments were made. In each case 0.100 g. of platinum-oxide catalyst was placed in 10 cc. of water and shaken with hydrogen until the brown oxide was reduced to black platinum. Then 5 g. of 2-benzoylpyridine, together with the indicated excess of hydrochloric acid was added, with enough water to make the total volume given in the table. Each sample of catalyst was taken from the same lot of freshly prepared catalyst, and the same initial hydrogen pressure (41 lb.) was used in each case. The results that were obtained are shown in Table I.

TABLE I

THE REDUCTION OF 2-BENZOYLPYRIDINE WITH VARYING AMOUNTS OF HYDROCHLORIC ACID

Excess of hydrochloric acid, %	Total volume of solution. cc.	Time of reduction. hours
10	45	13
10	75	No reduction
25	75	7.5
50	75	5.5
75	75	5
100	75	4
125	75	4
150	75	11.5

It is seen from the above data that 100–125% excess of hydrochloric acid over that necessary to form the hydrochloride is the optimum amount of acid for the reduction of this concentration of 2-benzoylpyridine. It is also apparent from the first two runs that a dilution from 45 cc. to 75 cc. of the benzoylpyridine hydrochloride solution containing a 10% excess of hydrochloric acid causes sufficient hydrolysis of the hydrochloride to the free base to prevent the reduction. In this connection it may be of interest to point out that Craig and Hixon[6] found that pyrrole could be more efficiently reduced to pyrrolidine in the presence of an excess of hydrochloric acid.

The two diastereoisomeric phenyl-2-piperidylcarbinols designated as A and B were separated as follows: 10 g. of 2-benzoylpyridine was reduced in 100% excess of hydrochloric acid, the catalyst filtered off and the water removed by evaporation under diminished pressure. The residual hydrochloride was recrystallized by dissolving in 5 cc. of absolute alcohol for each gram of hydrochloride and precipitating with 6 cc. of dry ether for each cc. of alcohol used. Four such recrystallizations gave 4.04 g. of the hydrochloride of A, m. p. 200–202°. On dissolving in a small amount of water and making alkaline with sodium hydroxide, 3.26 g. of the free base was obtained. One recrystallization from water containing 4% of alcohol gave 2.5 g. of A, m. p. 141–142°.

Anal. Subs., 0.2377, 0.2000: CO_2, 0.6544. 0.5514: H_2O, 0.1921, 0.1617. Calcd. for $C_{12}H_{17}ON$: C, 75.39; H, 8.90. Found: C, 75.08, 75.19; H, 8.98, 8.98. 0.6119 g. (1 mol) of this carbinol reacted with 0.6555 g. (2.01 mols) of acetic anhydride.?

The alcohol-ether filtrate from the first recrystallization of the hydrochloride of A contains most of the hydrochloride of B, the latter of which is the more soluble. On evaporation of the solvent and conversion to the free base, there remained 3.75 g. of base. After three recrystallizations of the free base from the minimum quantity of water containing 4% of alcohol, 0.81 g. of B, m. p. 171–173°, was obtained.

Anal. Subs., 0.2210, 0.2098: CO_2, 0.6086, 0.5805: H_2O, 0.1808. 0.1700. Calcd. for $C_{12}H_{17}ON$: C, 75.39; H, 8.90. Found: C, 75.10, 75.46; H, 9.09, 9.00. 0.4865 g. (1 mol) of the carbinol reacted with 0.4899 g. (1.89 mols) of acetic anhydride.

Evaporation of all filtrates from the purification of A and B and conversion to the free base gave 4.6 g., from which an additional quantity of A and B could be recovered by a repetition of the above method of separation.

Conversion of A into B.—One-half gram of A was heated at 100° for forty-eight

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[6] Craig and Hixon, THIS JOURNAL, 52, 804 (1930).

[7] The carbinol and a 3- to 4-fold excess of acetic anhydride contained in a sealed tube were heated overnight on a steam-bath, then dissolved in water and the excess acetic acid titrated with standard potassium hydroxide.

hours in 5 cc. of 25% hydrochloric acid. The solvent was removed under diminished pressure and the hydrochloride converted to the free base with sodium hydroxide. After three recrystallizations from water containing 4% of alcohol, there remained 0.032 g. of the B isomer that melted at 171–173°.

Phenyl-3-piperidylcarbinol Hydrochloride.—Ten grams 3-benzoylpyridine hydrochloride was reduced in aqueous solution with 0.5 g. of platinum-oxide platinum black catalyst. The reduction required fifteen hours for completion. After filtering off the catalyst and removing water under diminished pressure, the hydrochloride was purified by recrystallization from an alcohol–ether mixture. After five recrystallizations, 3 g. of product, m. p. 190–192°, was obtained.

Anal. Subs., 0.3558, 0.4267: AgCl, 0.2241, 0.2680. Subs., 0.2715: CO_2, 0.6338; H_2O, 0.1805. Calcd. for $C_{12}H_{18}ONCl$: Cl, 15.58; C, 63.30; H, 7.91. Found: Cl, 15.58, 15.54; C, 63.67; H, 7.56.

Phenyl-4-piperidylcarbinol Hydrochloride.—A solution of 10 g. of 4-benzoylpyridine hydrochloride in water absorbed the theoretical quantity of hydrogen in five hours when shaken with 0.5 g. of catalyst. After removal of solvent and one recrystallization from an alcohol–ether mixture, 10.2 g. of phenyl-4-piperidylcarbinol was obtained; m. p. 191–193°.

Anal. Subs., 0.2821, 0.3207: AgCl, 0.1768, 0.2016. Calcd. for $C_{12}H_{18}ONCl$: Cl, 15.58. Found: Cl, 15.50, 15.55.

Phenyl-4-piperidylcarbinol.—Ten grams of **phenyl-4-piperidylcarhinol** hydrochloride on conversion to the free base gave, after one recrystallization from water containing 4% of alcohol, 6.4 g. of the free base, m. p. 166–167°.

Anal. Subs., 0.2469, 0.2150: CO_2, 0.6805, 0.5936: H_2O, 0.2005, 0.1736. Calcd. for $C_{12}H_{17}ON$: C, 75.39; H, 8.90. Found: C, 75.17, 75.30; H, 9.02, 8.97. 0.9545 g. (1 mol) of the carbinol reacted with 1.004 g. (1.97 mols) of acetic anhydride.

Summary

1. The isomeric phenylpiperidylcarbinols have been prepared and described. In the case of the phenyl-2-piperidylcarbinol the two diastereoisomers have been isolated.

2. These carbinols have structures analogous to ephedrine and it has been found that although they are somewhat less active they all possess the same pharmacological properties as this important drug.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, UNIVERSITY OF BRISTOL]

A NEW METHYLATION PROCESS

BY M. NIERENSTEIN

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The catechins are remarkable for their well-crystallizing and sharp-melting penta-acetyl derivatives.[1] On the other hand, the corresponding methoxy derivatives, if prepared in the usual way by the action of dimethyl sulfate and alkali, either on the catechins themselves, or on the penta-acetyl derivatives, are contaminated with by-products, formed through fission of the chromane-ring.[2] It was therefore desirable to evolve a reliable method for the conversion of these well-defined penta-acetyl derivatives into the corresponding methoxy derivatives; such a method has now been elaborated. It consists in the interaction in the cold of diazomethane with these penta-acetyl derivatives in the presence of piperidine. The reaction proceeds smoothly and is easily controlled, each molecular proportion of piperidine removing one acetyl group, which is then replaced by the methyl group. The results obtained with the penta-acetyl catechins will be dealt with later on, a few representative cases being meanwhile described.

Experimental

The acetyl derivatives used in the following experiments were dissolved in alcohol and to this solution was added piperidine, also in alcoholic solution. Into this solution was then distilled an ethereal solution of diazomethane prepared from nitrosomethylurethan, the reaction being carried out in the apparatus previously described.[3] After standing for twenty-four hours the alcohol was removed, the solid dissolved in warm aqueous alkali and refluxed for thirty minutes on a water-bath. The methoxy derivatives were obtained by acidifying the cold solution, which had previously been freed from piperidine by exhaustive extraction with ether.

(1) Veratric Acid.—One gram of diacetyl-protocatechuic acid (m. p. 162°)[4] was reacted on with diazomethane from 5 cc. of nitrosomethylurethan in the presence of 1 g. of piperidine (excess); yield, 0.6 g.; m. p. and mixed m. p., 180°.

Anal. Subs., 2.107, 6.302 mg.: AgI, 5.365, 16.267 mg. Calcd. for $C_9H_{10}O_4$: OCH_3, 34.07. Found: OCH_3, 33.61.34.06.

(2) Isovanillic Acid—The same proportions as given above were used, with the exception of piperidine, when 0.4 g. (1 mol) was added; yield, 0.7 g.; m. p. 249°.

Anal. Subs. 4.085 mg.: AgI, 5.667 mg. Calcd. for $C_8H_8O_4$: OCH_3, 18.45. Found: OCH, 18.32.

(3) Dimethyl-β-resorcylic Acid.—One gram of diacetyl-β-resorcylic acid (m. p.

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[1] Nierenstein, J. Indian *Chem. Soc.*, 7, 279 (1930).

[2] Nierenstein, THIS JOURNAL, 48, 1964 (1926).

[3] Malkin and Nierenstein, *ibid.*, 52, 1508 (1930).

[4] Malkin and Nierenstein, *Ber.*, 61, 797 (1928).

137°)[5] was reacted on with diazomethane in the presence of 0.8 g. (2 mols) of piperidine; yield, 0.5 g.; m. p. 109°, which is in agreement with the melting point given by Liebermann and Lindenbaum.[6]

Anal. Subs., 3.314 mg.: AgI, 8.533 mg. Calcd. for $C_9H_{10}O_4$: OCH_3, 34.07. Found: OCH_3, 33.99.

(4) **Monomethyl-β-resorcylic** Acid.—When using one molecule of piperidine a mixture of the two monomethyl-β-resorcylic acids was obtained. This mixture melted gradually between 169 and 174°, and gave with ferric chloride a violet coloration which had a distinctly greenish tint. The two isomers in question show the following properties: 2-hydroxy-4-methoxybenzoic acid melts at 160-161°, and gives a violet coloration with ferric chloride, whereas 2-methoxy-4-hydroxybenzoic acid melts at 187-189°, and gives a red-brown coloration with ferric chloride. The former substance therefore predominated in the mixture.

Anal. Subs., 7.310 mg.: AgI, 10.571 mg. Calcd. for $C_8H_8O_4$: OCH_3, 18.45. Found: OCH_3, 19.08.

(5) **Trimethylgallic** Acid.—One gram of triacetylgallic acid (m. p. 175°)[7] was methylated in the presence of an excess of piperidine; yield, 0.8 g.; m. p. 169°, with slight evolution of carbon dioxide.

Anal. Subs., 4.017 mg.: AgI, 13.303 mg. Calcd. for $C_{10}H_{12}O_5$: OCH_3, 43.86. Found: OCH_3, 43.72.

Summary

A method is described for the replacement of acetyl groups by methyl groups, using diazomethane and piperidine.

BRISTOL, ENGLAND

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

LOCAL ANESTHETICS DERIVED FROM QUINOLINE AND ISOQUINOLINE

BY C. F. BAILEY AND S. M. MCELVAIN

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Several previous communications[1] from this Laboratory have described the preparation of substituted piperidino-alkyl benzoates and substituted piperidino-alkyl cinnamates. Since these compounds possessed local anesthetic action, some of them to a marked degree, it seemed desirable to prepare for pharmacological study a series of hydroquinolino-alkyl benzoates in which the nitrogen, instead of being a member of a piperidine ring, is incorporated in a bicyclic structure such as that present in certain of the reduced forms of quinoline and isoquinoline. It seemed of par-

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Bergmann and Dongschat. *Ber.*, 52, 179 (1919).

[6] Liebermann and Lindenbaum, *ibid.*, 41, 1613 (1908).

[7] Fischer, Bergmann and Lipschitz, *ibid.*, 51, 53 (1918), give m. p. 171-172° (corr.) for triacetylgallic acid.

[1] McElvain, THIS JOURNAL, 49, 2835 (1927); Thayer and McElvain, *ibid.*, 50, 3348 (1928); Bailey and McElvain, *ibid.*, 52, 1633 (1930); Bailey and McElvain, *ibid.*, 52, 2007 (1930).

ticular interest to ascertain whether or not there would be any marked pharmacological difference in the anesthetics derived from the stereoisomeric decahydroquinolines. Also an anesthetic derived from tetrahydroisoquinoline would possess a phenylene-dialkylamino structure and would be an interesting type to compare with those anesthetics containing phenyl alkyl groups which have been previously reported[2] as being unusually potent pharmacologically.

This paper describes the preparation, properties and pharmacological action of the hydrochlorides of the following amino esters: (1) β-tetrahydroquinolino-ethyl benzoate, (2) γ-tetrahydroquinolinopropyl benzoate, (3) *trans*-β-decahydroquinolino-ethyl benzoate, (4) *trans*-γ-decahydroquinolinopropyl benzoate, (5) *cis*-β-decahydroquinolino-ethyl benzoate, (6) cis-y-decahydroquinolinopropyl benzoate, (7) γ-tetrahydroisoquinolinopropyl benzoate. These compounds were prepared by the condensation of the corresponding secondary amines with (3-chloro-ethyl benzoate and γ-chloropropyl benzoate.

Tetrahydroquinoline was prepared by the catalytic reduction of quinoline. The cis and trans isomers of decahydroquinoline were prepared by the complete catalytic reduction of quinoline; the reduced material obtained in this manner was separated into the pure isomeric forms by a modification of the method of Hiickel and Stepf.[3] The literature contains numerous references to the trans isomer (m. p. 48°)[4] but the existence of the cis isomer, which is a liquid at ordinary temperatures, had not been demonstrated previous to the work of Hiickel and Stepf.

Tetrahydroisoquinoline was prepared by the method of Pictet and Spengler,[5] which involves the condensation of methylal and β-phenylethylamine in concentrated hydrochloric acid solution. The tetrahydroisoquinoline so obtained was not entirely pure, and it was observed that the strength of the hydrochloric acid used in the condensation plays an important part in determining the course of the reaction. In dilute acid solution methyl-(3-phenylethylamine, instead of tetrahydroisoquinoline, is formed.

Experimental

Tetrahydroquinoline.—This compound was prepared by the catalytic reduction of quinoline, using a nickel catalyst at a temperature of 150° and at pressures of 150–170 atmospheres of hydrogen.6 The boiling point of the product was 122–124° (10 mm.)

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[2] Thayer and McElvain, THIS JOURNAL, 49,2862 (1927); Bolyard and McElvain, *ibid.*, *51*, 922 (1929); Bailey and McElvain, *ibid.*, 52, 1633 (1930).

[3] Hiickel and Stepf, *Ann.*, 453, 163 (1927).

[4] Bamberger and Lengfeld, *Ber.*, 23, 1145 (1890); Ipatieff, *ibid.*, 41, 992 (1908); Skita and Meyer, *ibid.*, 45, 3593 (1912).

[5] Pictet and Spengler, *ibid.*, 44, 2030 (1911).

[6] The reduction of quinoline was carried out by Mr. Howard Cramer under the direction of Professor Homer Adkins and will be described in detail by them in a forthcoming paper.

***Trans*- and *Cis*-decahydroquinoline.**—Quinoline was completely reduced catalytically, using a nickel catalyst at a temperature of 200° and at pressures of 150–200 atmospheres of hydrogen. The relative proportions of cis and trans isomers varied in different runs. By chilling with ice–salt mixture the trans isomer crystallized and, after filtering with suction and pressing on a clay plate to remove adhering liquid, it melted at 48°.[4] The hydrochloride melted at 278–279°; Hiickel and Stepf report 275' as the melting point of this compound.

The crude cis-demhydroquinoline remaining after removal of the *trans* isomer was converted to the benzoyl derivative by treatment with benzoyl chloride and dilute alkali. Hiickel and Stepf[3] recommended partial purification of the hydrochloride before preparation of the benzoyl derivative, but it was found that better yields were obtained by making the benzoyl derivative directly from the crude base. After two recrystallizations from ligroin (b. p. 90–150°) the material was pure, melting at 969 From 97 g. of crude base there was obtained 45.3 g. of the pure benzoyl-*cis*-decahydroquinoline.

Continued refluxing with 15% sodium hydroxide solution did not hydrolyze benzoyl-cis-decahydroquinoline, but it was found that by refluxing with 20% hydrochloric acid, hydrolysis was complete after sixty to seventy hours. At the end of this time the solution was cooled, after which benzoic acid was filtered off and the filtrate was evaporated on a steam-bath. The free base was liberated with 10% sodium hydroxide and extracted with ether. After drying the ethereal solution with sodium sulfate, the ether was evaporated and the amine was distilled under diminished pressure. By such treatment of 45 g. of benzoyl-*cis*-decahydroquinoline there was obtained 21.9 g. (85% of the theoretical) of cis-decahydroquinoline which boiled at 83–83.5° (16 mm.). The hydrochloride was prepared and found to melt at 222–224°; Hiickel and Stepf reported 226° as the melting point of this compound.

Tetrahydroisoquinoline.—This compound was prepared by a modification of the method of Pictet and Spengler.[5] To a solution of 20 g. of β-phenylethylamine (b. p. 85–88° at 14 mm.) in 120 cc. of concentrated hydrochloric acid, 20 g. of methylal (b. p 41–45°) was slowly added through a separatory funnel. During the addition the reaction mixture was warmed on a steam-bath. Heating was continued for five hours, after which the solution was evaporated to dryness. The residue was dissolved in 90 cc. of water; to this solution, cooled to 7°, was added a solution of 23 g. of sodium nitrite in 40 cc. of water. The mixture was warmed and extracted with ether. After evaporation of the ether, the nitrosamine was reduced with 33 g. of zinc and 90 cc. of concentrated hydrochloric acid. The mixture was made alkaline with 60 g. of sodium hydroxide and steam distilled until all of the oily layer had passed over. The distillate was acidified and evaporated to dryness; the residue was made alkaline, and the free base was extracted with ether. After drying with sodium sulfate and evaporating the ether, the amine was distilled. The yields were 2.2–3 g. (10–14% of the theoretical) of material boiling at 220–233°. The picrate after two recrystallizations from alcohol melted at 199–200°; Helfer[7] reported 197–198° as the melting point of tetrahydroisoquinoline picrate. The hydrochloride after five recrystallizations from alcohol–ether melted at 194–195"; Helfer[7] reported 195–196°.

In an attempt to improve the yield of tetrahydroisoquinoline a run was made using 120 cc. of dilute hydrochloric acid containing only slightly more hydrogen chloride than the amount required to dissolve the β-phenylethylamine. The time of heating was seventeen hours; the rest of the procedure was that described above; 3 g. (14%) of material boiling at 88–95' (16 mm.) was obtained. This was shown to be methyl-β-

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[7] Helfer, *Helv. Chim. Acta*, 6, 794 (1923).

phenylethylamine.[8] The picrate was prepared and found to melt at 140–141°;[9] a mixed melting point with an authentic specimen of methyl-β-phenylethylamine picrate showed no depression.

Hydroquinolino-alkyl Benzoates.—These compounds were prepared by the general procedure of heating two moles of the secondary amine with one mole of β-chloro-ethyl benzoate or γ-chloropropyl benzoate. In the case of the decahydroquinolines a temperature of 140–150° for two to three hours was sufficient to cause a satisfactory reaction; in the case of tetrahydroquinoline and tetrahydroisoquinoline a somewhat higher temperature (190–200°) for the same period of time was required. The tertiary amino esters were isolated as the hydrochlorides by the procedure commonly employed for compounds of this type.[1] These hydrochlorides are summarized in Table I.

In the case of *trans*-β-decahydroquinolino-ethyl benzoate hydrochloride two apparently isomeric substances appeared to be formed. One of them was obtained pure, while the other could not be caused to attain a constant melting point. Theoretical chlorine analyses for samples melting over a wide temperature range was the evidence upon which the formation of isomers was based.

TABLE I

HYDROQUINOLINO-ALKYL BENZOATE HYDROCHLORIDES

	Hydroquinolino-alkyl group	M. p., °C.	Analyses, Cl, % Calcd.	Found
1	β-Tetrahydroquinolino-ethyl[a]	129–131	11.18	11.18
2	γ-Tetrahydroquinolinopropyl[a]	122–124	10.71	11.04
3	*Trans*-β-decahydroquinolino-ethyl[b]	155–157	10.97	10.87
4	*Trans*-γ-decahydroquinolinopropyl	171–173	10.52	10.51
5	*Cis*-β-decahydroquinolino-ethyl[b]	159–160	10.97	10.82
6	*Cis*-γ-decahydroquinolinopropyl	155–156.5	10.52	10.38
7	γ-Tetrahydroisoquinolinopropyl[c]	188–189	10.71	10.64

[a] These hydrochlorides are sufficiently hydrolyzed in aqueous solution to cause oily globules of free base to appear. [b] A mixed melting point on Nos. 3 and 5 was 135–141°. [c] The corresponding propyl benzoate derived from methyl-β-phenylethylamine melts at 128°; this compound has been prepared by Mr. A. C. Cope in this Laboratory and will be described in a future communication.

Pharmacological Report.—These compounds are being studied pharmacologically by Mr. Charles L. Rose of The Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana. Table II contains a brief summary of this work. Each compound is designated by the number which is associated with it in Table I. Anesthetic efficiencies were determined by application of a 2% solution of the hydrochloride to the rabbit's cornea and noting the duration of anesthesia and also by the method of infiltration anesthesia, which involves the intracutaneous injection of a 1% solution of the hydrochloride into the guinea pig. Subcutaneous toxicity to white mice and intravenous toxicity to white rats were determined; these values are reported in terms of the median lethal dose (M. L. D.), which is that amount of material necessary to cause the death

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[8] *Cf.* Decker and Becker, Ber., **45**, 2404 (1912); Decker and Becker, *Ann.*, **395**, 342 (1913).

[9] Johnson and Guest, Am. Chem. J., **42**, 340 (1909).

of 50% of a large number of animals.[10] The values for cocaine and procaine are included in Table II for comparison.

β-Tetrahydroquinolino-ethyl benzoate (1) and γ-tetrahydroquinolinopropyl benzoate (2) were hydrolyzed to such an extent that a solution could not he prepared for pharmacological tests. Hence there are no data for these compounds in Table II.

TABLE II

PHARMACOLOGICAL DATA

Compound	Av. duration of anesthesia, min. Rabbit's cornea	Infiltration	Subcutaneous toxicity to white mice mg./kg. M. L. D.	No of mice used	Intravenous toxicity to white rats mg./kg. M. L. D.	No. of rats used
3	5	36	1000	25	25	7
4	27	81	500	40	20	24
5	21	55	700	36	30	14
6	30	60	500	25	20	15
7	7	187	1600	31	40	10
Cocaine	29	..	150	..	17.5	..
Procaine	0	..	800	..	53	..

Discussion of the Pharmacological Data.—The decahydroquinolinoalkyl benzoates are in general more satisfactory anesthetics than cocaine, since the anesthetic efficiencies of three of them are equal, or nearly equal, to that of cocaine, while the toxicities are considerably less than that of cocaine. Compounds 4 and 6, which are geometric isomers, have quite similar properties. However, 3 and 5, which are also geometric isomers, differ from each other considerably—5, the cis compound, being more active than 3, its *trans* isomer, both as regards anesthetic action and toxicity.

γ-Tetrahydroisoquinolinopropyl benzoate[7] has quite a low toxicity combined with high anesthetic efficiency when measured by the infiltration method. However, when measured by the corneal method, the anesthetic efficiency is quite low. The compound contains a phenylene-dialkylamino structure, and would therefore be expected to be a rather powerful anesthetic on account of its structural relationship to those anesthetics containing phenyl alkyl groups.[2] It is reported as being highly irritating to the rabbit's cornea, and it is quite probable that it is this property rather than its structure, which causes the low corneal anesthesia value.

Summary

1. A series of hydroquinolino-alkyl benzoates has been prepared and described.
2. A discussion of the pharmacological properties of these compounds is given.

MADISON, WISCONSIN

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[10] Rose, Coles and Thompson, *J. Lab. Clin. Med.*, 15, 731 (1930).

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

DI-IODOTHYMOL AND THE DECOMPOSITION OF ITS SALTS[1]

BY G. H. WOOLLETT AND CARL H. EVERETT

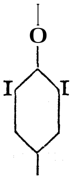
RECEIVED JUNE 25, 1930 PUBLISHED OCTOBER 6, 1930

Colored products obtained by the action of iodine and alkali upon phenols have been described by various investigators.[2] The deep red product formed from common phenol[2d] has been shown to consist largely of material having a high apparent molecular weight and quinonoid characteristics. Its formation from phenol takes place according to the equations

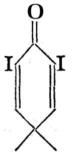
$$C_6H_5OH + 4NaOH + 3I_2 = C_6H_2I_3ONa + 3NaI + 4H_2O \qquad (I)$$

$$n\,C_6H_2I_3ONa + I_2 = (C_6H_2I_2O)_n + n NaI + I_2 \qquad (II)$$

During the action represented by Equation II, divalent radicals such as



or



or the ortho isomers are probably formed, the final product being made by their polymerization. Substances of this type are amorphous, soluble in carbon disulfide or bromoform, and insoluble in alcohol, water and ligroin, lose their color on reduction and regain it upon re-oxidation. They will be referred to here as chromo-resinoids.

Probably the best known of these substances is the one obtained from thymol, as it is, in an unpurified state, used as the pharmaceutical now called thymol iodide. The similarity in preparation and properties strongly suggest for the thymol chromo-resinoid a genesis similar to that of its phenol analog. This would require the formation and subsequent decomposition of di-iodothymol. Previous work[3] also pointed in this direction. As no description of a di-iodothymol could be found in the literature, an attempt was made to prepare it.

Willgerodt and Kornblum[4] and later Rasik Lal Datta and Nogendra Prosad[5] have iodinated phenols in ammoniacal solution, the former using alcohol as a solvent and the latter the alkali salts of the phenols.

It was found possible to introduce a second iodine atom into *p*-iodothymol by a modification of these methods using no solvent other than the

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[1] A portion of this work formed part of a thesis presented to the Faculty of the Graduate School of the University of Mississippi by Carl H. Everett in partial fulfilment of the requirements for the degree of Master of Science.

[2] (a) Lautemann, Ann., 120, 309 (1861); (b) Kammeier and Benzinger, *Ber.*, 11, 557 (1878); (c) Messinger and Vortmann, *ibid.*, 22,2312 (1889); (d) Hunter and Woollett, THIS JOURNAL, 43, 135 (1921); (e) Vortmann, *Ber.*, 56,234 (1923); and others.

[3] Woollett, THIS JOURNAL, 43, 553 (1921).

[4] Willgerodt and Kornblum, *J. prakt.* Chem., [2] 39,290 (1889).

[5] Rasik Lal Datta and Nogendra Prosad, THIS JOURNAL, 39,441 (1917).

ammonia solution. The di-iodothymol made thus is a straw-colored liquid which did not solidify at −17°. It forms a crystalline benzoate (m. p. 112°). The second iodine atom is presumably ortho to the hydroxyl. Because of the repeated reports of dimolecular structures for iodothymol derivatives, the molecular weight of the benzoate was taken and found to be normal.

Di-iodothymol decomposes spontaneously, giving the expected red resinoid when treated with sodium hydroxide solution. The decomposition appears to start at the surface of undissolved droplets of the phenol and once initiated goes a great way toward completion. As alcohol, acetone, sulfites or other substances which react easily with iodine prevent the decomposition, and as free iodine in catalytic quantity will cause decomposition in undecomposed alkaline solutions, the spontaneous decomposition is believed to be due to traces of free iodine in the di-iodothymol.

Potassium ferricyanide also will cause the formation of a chromo-resinoid apparently identical with the above. The action in this case is not catalytic but requires molecular quantities of ferricyanide and will take place in the presence of considerable antagonistic material such as sulfites.

As might be expected from its method of preparation, U. S. P. thymol iodide contains a demonstrable amount of di-iodothymol, as shown by the action of potassium ferricyanide on alcoholic extracts from it.

While tri-iodophenol seldom decomposes on mere contact with alkali, its behavior otherwise is remarkably like that of di-iodothymol.

Experimental

Preparation of *p*-Iodothymol.—Eight hundred cc. of 0.25 molecular sodium thymolate and 0.25 molecular I_2–KI solution were run slowly and at approximately equal rates into a 12-cm. funnel filled with cracked ice. The funnel discharged into a 3-liter beaker containing cracked ice and 500 cc. of water, mechanically stirred.

When about one-tenth of the reactants had been added, the product was seeded with iodothymol and addition was interrupted until crystallization started. Excess of iodine present at the end was removed by sodium bisulfite.

The white crystalline p-iodothymol (51.5g.) was filtered off and purified by dissolving twice in alkali, treating with norit, and precipitating by dilute sulfuric acid; then by twice dissolving in alcohol, treating with norit, filtering and precipitating by water; and finally by two crystallizations from heptane (m. p. 69°). Willgerodt[4] gives the melting point as 69°.

Preparation of Di-iodothymol.—One gram of pure p-iodothymol was dissolved in 800 cc. of concd. ammonia. To this was added rapidly and with shaking 20 cc. of 0.2 *M* iodine–potassium iodide solution. After one minute 1 cc. of 20% sodium bisulfite was added and the mixture was poured into a previously prepared bottle containing 500 cc. of ice water and 150 cc. of ether. The di-iodothymol was extracted twice and the ether allowed to evaporate spontaneously. Steam was passed through the remaining yellowish oil to remove iodothymol. The non-volatile residue was taken up in a small amount of acetone and then added to 200 cc. of water containing 5 cc. of 4 *N* sodium hydroxide, boiled to remove acetone, cooled, 1 g. of norit added and filtered. The filtrate contained nearly pure di-iodothymol, which was precipitated by dilute sulfuric acid, extracted with ether and dried over sodium sulfate. After evaporation of the ether, a light yellow oil was left which failed to solidify after several days at −17°; average yield, 0.63 g. or 43%.

Anal. (Carius). Calcd. for $C_{10}H_{12}I_2O$: I, 63.17. Found: I, 62.92, 62.85. 62.92.

Preparation of Di-iodothymol Benzoate.—A solution of 2 g. of di-iodothymol was made as above. cooled and shaken with 20 cc. of benzoyl chloride and 70 cc. of 4 *N* alkali. The insoluble material was washed with alkali and water, dried and crystallized three times from alcohol and four times from heptane. The last two crystallizations gave colorless crystals of constant melting point (112").

Anal. (Carius). Calcd. for $C_{17}H_{16}I_2O_2$: I, 50.18. Found: I, 50.03, 49.97. *Mol. wt.* (cryoscopically in benzene). Calcd. for $C_{17}H_{16}I_2O_2$: 506.05. Found: 429,447.

Decomposition by Alkali.—Samples I to IV of di-iodothymol were stirred up with sodium hydroxide solution. They turned red and became semi-solid. Water was then added, and the precipitates were filtered off, washed. dried and extracted with alcohol to remove undecomposed di-iodothymol. The chromo-resinoid, alcoholic extract and silver iodide precipitated from the filtrate with silver nitrate were all weighed. The chromo-resinoid was analyzed for iodine.

TABLE I

No.	Sample. g.	Undecomposed, g.	Amount decomposed, g.	Iodine removed. g.	%	Chromo-resinoid ($C_{10}H_{11}IO)_n$ formed, g.	%	Iodine in resinoid (Carius), %
I	0.7626	0.1230	0.6392	0.1507	33.4	0.4515	70.8	47.34
II	1.7615	.1574	1.6041	0.5006	31.21	1.0962	68.3	44.26
III	0.6794	...	0.5002 (calcd.)	0.1655	33.1	0.341		44.93
IV	0.9796	...	0.6734 (calcd.)	......		0.4537		46.35
Calculated values..................					31.58		68.17	46.32

Decomposition by Other Means.—Samples V to VIII of di-iodothymol were put in solution in alkali using acetone as a protective agent. This was later removed by boiling. The resinoids formed were not extracted to remove undecomposed di-iodothymol.

TABLE II

Samples V and VI were caused to decompose by adding small amounts of iodine in solution.

No.	Sample, g.	Iodine added, g.	Chromo-resinoid ($C_{10}H_{11}IO)_n$ formed g.	%	Iodine in resinoid (Carius), %
V	0.6667	0.05	0.4800	72.00	47.17
VI	1.0343	.29	.7271	70.30	...

Samples VII and VIII were treated with $K_3Fe(CN)_6$ solution.

		N/10 $K_3Fe(CN)_6$, cc.			
VII	0.6631 (0.00140 mole)	14.8 (0.00148 mole)	0.3777	67.08	46.36
VIII	1.1515 (0.00286 mole)	31.1 (0.00311 mole)	0.8245	71.80	47.73

Di-iodothymol from U. S. P. Thymol Iodide.—A sample was extracted with methanol. Water and a little sodium bisulfite were added to the alcoholic extract and steam was passed through to remove methanol, thymol and iodothymol. The residue was dissolved in 5 cc. of acetone and dilute sodium hydroxide added. The acetone was removed by boiling, the alkaline solution treated with norit and filtered. A solution containing 2 g. of potassium ferricyanide was added to the cold filtrate and the typical red resinoid was filtered off, dried and weighed: sample, 4.372 g.; chromo-resinoid 0.113 g., corresponding to 3.7% di-iodothymol.

Anal. (Carius). Calcd. for $(C_{10}H_{11}IO)_n$: I, 46.32. Found: 1, 44.75.

Summary

Di-iodothymol and its benzoate have been prepared.

Di-iodothymol salts have been shown to be precursors of the chromo-resinoid formed when iodine acts on alkaline solutions of thymol according to the equation $nC_{10}H_{11}I_2ONa = (C_{10}H_{11}IO)_n + n\ NaI$.

Di-iodothymol has been shown to be present in U. S. P. thymol iodide.

UNIVERSITY, MISSISSIPPI

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

THE POLYMERIZATION OF ASYMMETRICAL DIPHENYLETHYLENE. THE PREPARATION OF 1,1,3-TRIPHENYL-3-METHYLHYDRINDENE

BY C. S. SCHOEPFLE AND J. D. RYAN[1]

RECEIVED JUNE 30, 1930 PUBLISHED OCTOBER 6, 1930

Bergrnann and Weiss, in a paper recently published,[2] have shown that the saturated dimer of asymmetrical diphenylethylene is 1,1,3-triphenyl-3-methylhydrindene and not tetraphenylcyclobutane, as previously supposed, and have stressed the importance of this fact in connection with the views of Staudinger and others on the mechanism of polymerization and the structure of high molecular weight compounds. In a study of the properties of this saturated dimer in this Laboratory, its identity has been established, independently, from its oxidation products. Our investigation, which is still in progress, is concerned chiefly with the mechanism of the reaction by which triphenylmethylhydrindene and other indenes are formed, but the work has paralleled that of Bergmann and Weiss in many respects and therefore it is considered advisable to publish the results which have been obtained at this time.

Polymerization of asymmetrical diphenylethylene (I) by the use of catalysts yields two dimeric compounds, one unsaturated (III) and the other saturated (XII). The unsaturated dimer, m. p. 113°, was prepared first by Hildebrand[3] and shown by Lebedev[4] to be 1,1,3,3-tetraphenyl-1-butene,

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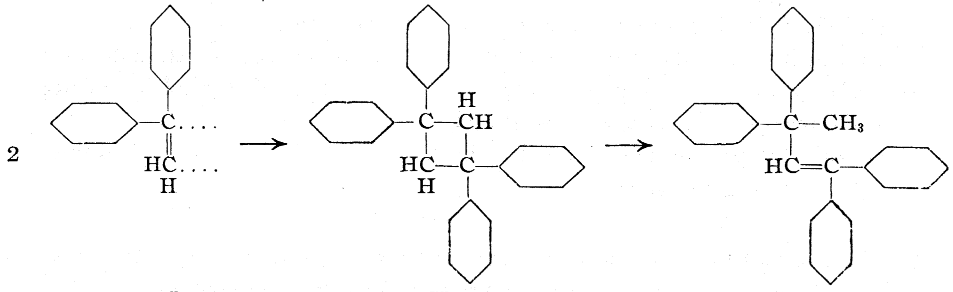
[1] This paper represents part of a dissertation to be submitted to the Graduate School by Mr. Ryan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] Bergmann and Weiss, Ann., 480, 49 (1930).

[3] Dissertation by Hildebrand, Strassburg, 1909.

[4] Lebedev, Andreevskii and Matiushkina, Ber., 56,2349 (19%).

which structure was confirmed by Schlenk and Bergmann.[5] The formation of this compound may be explained by assuming that two molecules of asymmetrical diphenylethylene combine under the influence of catalysts such as sulfuric acid, iodine, stannic chloride, etc., to give 1,1,3,3-tetraphenylcyclobutane (11), which being unstable rearranges to 1,1,3,3-tetraphenyl-1-butene (III). The intermediate product cannot be 1,1,4,4-tetraphenylcyclobutane, since it appears from the work of Schlenk and Bergmann[6] that this compound, prepared by the action of mercury on 1,4-disodium-1,1,4,4-tetraphenylbutane, reverts to diphenylethylene.



I II III

The saturated dimer, m. p. 143°, was prepared first by Lebedev,[4] who obtained a mixture of the two isomers by treating diphenylethylene with concentrated sulfuric acid or with fuller's earth. He concluded that this compound was tetraphenylcyclobutane, since it did not add bromine nor react with ozone, and gave only benzophenone on oxidation. The compound is very stable toward oxidation and Bergmann and Weiss state that long treatment with a considerable excess of chromic acid in acetic acid oxidized only a part of the material and that this part was completely destroyed. By regulating the conditions of the oxidation, however, it is possible to control the reaction so that over a 40% yield of the crude oxidation product is obtained. This product contains a large number of acids and ketones of which about ten have been isolated in pure form. Only two of these were readily identified, namely, benzoic acid and o-dibenzoylbenzene. In addition, benzophenone was isolated as the oxime in small amounts, substantiating the observation of Lebedev. The two latter oxidation products were sufficient to establish the identity of the hydrocarbon, since of the various structures which might be assigned to a dimer of diphenylethylene, only one, namely, 1,1,3-triphenyl-3-methylhydrindene could give both *o*-dibenzoylbenzene and benzophenone on oxidation and could readily be formed by the rearrangement of 1,1,3,3-tetraphenyl-1-butene, which rearrangement had been effected by Lebedev[4]

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[5] **Schlenk and Bergmann, Ann., 463, 239 (1928).**

[6] **Ref. 5, p. 7.**

with fuller's earth at high temperature and with stannic chloride plus hydrochloric acid at room temperature in our work. A synthesis of this hydrindene was in progress at the time when Bergmann and Weiss[2] reported their excellent synthesis, which removed any possible doubt concerning its structure.

1,1,3-Triphenyl-3-methylhydrindene can be readily prepared in practically quantitative yield by adding anhydrous stannic chloride to a benzene solution of methyldiphenylchloromethane, obtained by the action of dry hydrogen chloride on the corresponding carbinol, and allowing the mixture to stand at room temperature for one week. The reaction is apparently a general one and has been extended to several other carbinol chlorides. For example, dimethylphenylchloromethane gave the dimer, m. p. 52.5°, first described by Grignard,[7] and dimethyl-*p*-tolylchloromethane and dimethyl-a-naphthylchloromethane gave compounds melting at 122 and 199°, respectively.[8] The structures of these compounds remain to be proved. Zinc chloride, ferric chloride, antimony pentachloride and aluminum chloride have been used in the reaction in place of stannic chloride, and it is probable that other agents such as boron trichloride and titanium tetrachloride will also be effective.

Inasmuch as tetraphenylbutene can be rearranged to the hydrindene by concentrated sulfuric acid at room temperature, it seems probable that the former is an intermediate step in the preparation of the latter compound from diphenylethylene. As suggested by Bergmann and Weiss, the rearrangement of the unsaturated dimer would consist in the addition of the sulfuric acid to the double bond and the subsequent removal of the acid to form the stable five-membered ring. The unsaturated dimer may also be rearranged by means of stannic chloride, provided hydrogen chloride is present. A benzene solution of this compound in the presence of stannic chloride showed no appreciable rearrangement after one week at room temperature, but when the solution was partially saturated with hydrogen chloride, the rearrangement to the saturated dimer was practically complete in the same period of time. Again, diphenylethylene in benzene solution under the influence of stannic chloride polymerized almost exclusively to the unsaturated dimer, while in the presence of hydrogen chloride the saturated isomer was formed. These results apparently favor the theory that an intermediate compound is formed by the addition of hydrogen chloride to the unsaturated dimer, which compound then reacts to give the hydrindene, but there is some evidence which points to a different mechanism of reaction when stannic chloride is used.

If the preparation of 1,1,3-triphenyl-3-methylhydrindene from methyl-

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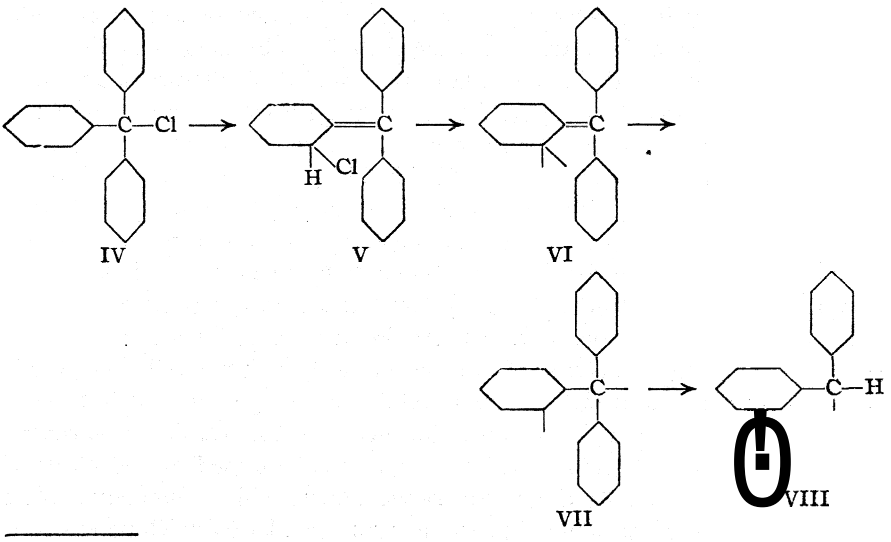
[7] Grignard, "Ann. de l'Univ. of Lyon," **1901, p.** 57; ***Ann. chim. phys.,*** [7] **24,** 485 (1901).

[8] These compounds were prepared by R. F. Ruthruff.

diphenylchloromethane is compared with the preparation of fluorenes from triarylmethyl halides, it is found that the two reactions have much in common. In each case the product is an indene derivative, and in each case the same reagents may be used to bring about the reaction, namely, stannic chloride, aluminum chloride, zinc chloride, etc. These reagents incidentally give definite colored addition products with the triarylmethyl halides which have been shown to be quinonoid in character.[9] The ease with which fluorenes are formed from triarylmethyl halides varies greatly with different individuals. Triphenylmethyl chloride and bromide give phenylfluorene (VIII) only upon heating above 200°.[10] Phenyl-α-naphthofluorene, however, may be prepared by refluxing an acetic acid solution of α-naphthyldiphenylcarbinol in the presence of a small amount of hydrochloric acid, sulfuric acid, zinc chloride, etc.;[11] the solution first acquires a dark green color which rapidly disappears, indicating that the intermediate product is a quinonoid chloride, sulfate, etc. Di-α-naphthylphenylmethyl chloride or bromide is still more reactive. These halides give addition products of a deep purple color with stannic, aluminum, ferric, zinc and mercuric chlorides, which are unstable and decompose within a short time at room temperature with the formation of di-α-naphthofluorene.[12]

The reaction, for example, in the case of triphenylchloromethane, probably takes place by splitting off the chlorine atom and a hydrogen atom



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[9] Gomberg, *Ber.*, *40*, 1847 (1907); 42, 406 (1909); Anderson, THIS JOURNAL, 52, November, 1930.

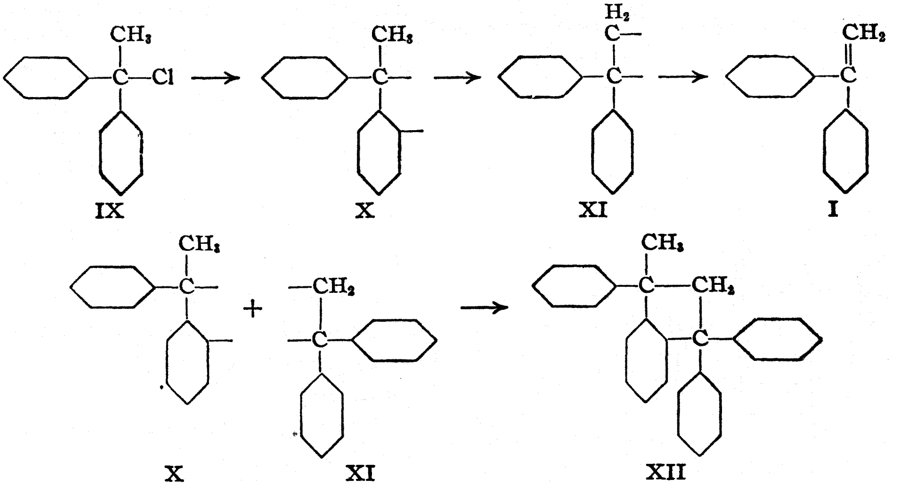
[10] Hemilian, *Ber.*, 7, 1208 (1874); 11, 837 (1878); E. and O. Fischer, Ann., 194, 257 (1878); Schwarz, *Ber.*, 14, 1522 (1878).

[11] Ullmann and Mourawiew-Winigradoff. *ibid.*, 38, 2213 (1905).

[12] Schoepfle, THIS JOURNAL, 44, 188 (1922).

from an ortho position in the ring to give an unstable intermediate product (VII) which rearranges to the stable fluorene (VIII). Since the reagents or the conditions used in the reaction result in quinoidation of the triarylmethyl halide, the formation of the intermediate compound (VII) may be postulated as being due to splitting off hydrogen chloride from the ortho quinonoid compound, (V), to give the quinonoid residue (VI), which would, of course, rearrange to the benzenoid configuration (VII). In general, the triarylmethyl halides assume the para-quinonoid form but some of the ortho-quinonoid form may also be present, and, indeed, certain compounds would be expected to assume the ortho-quinonoid form more readily than others, which might account for the greater ease with which naphthyl derivatives react in comparison with phenyl derivatives.

In the case of methyldiphenylchloromethane (IX), hydrogen chloride may be split off in accordance with the mechanism proposed above to give



the intermediate product (X), which then tends to rearrange not to methylfluorene but to asymmetrical diphenylethylene, a rearrangement which is not possible in the case of the triarylmethyl derivatives. Actually, however, the rearrangement does not proceed thus far, due to the coupling of the two intermediate products (X) and (XI) to give the stable triphenylmethylhydrindene.

Methyldiphenylcarbinol and concentrated sulfuric acid give a red color which is also characteristic of the addition compounds of methyldiphenylchloromethane with stannic chloride, aluminum chloride, ferric chloride, etc. In the polymerization of diphenylethylene to the hydrindene in the presence of stannic chloride and hydrochloric acid, and in the rearrangement of the unsaturated dimer under these conditions, the same red color always appears. In the absence of hydrochloric acid, the ethylene and the unsaturated dimer give a light green color instead of the red color and in each case practically no hydrindene is obtained. In other words, it seems that the preparation of the hydrindene may be dependent on the formation of methyldiphenylchloromethane as the intermediate product. The formation of this compound is readily explainable with the ethylene which may add hydrochloric acid under the influence of the stannic chloride, and is also plausible in the case of the unsaturated dimer, which evidently dissociates readily to the ethylene, since Hildebrand[8] found that bromine and nitric acid in boiling acetic acid react with the unsaturated dimer to give dibromodiphenylethylene and diphenylvinyl nitrite, respectively, while Lebedev[4] found that with excess of ozone at 0°, diphenylethylene ozonide was obtained from the dimer. Moreover, it was observed that the unsaturated dimer in benzene solution and in the presence of stannic chloride depolymerized to an appreciable extent at room temperature.

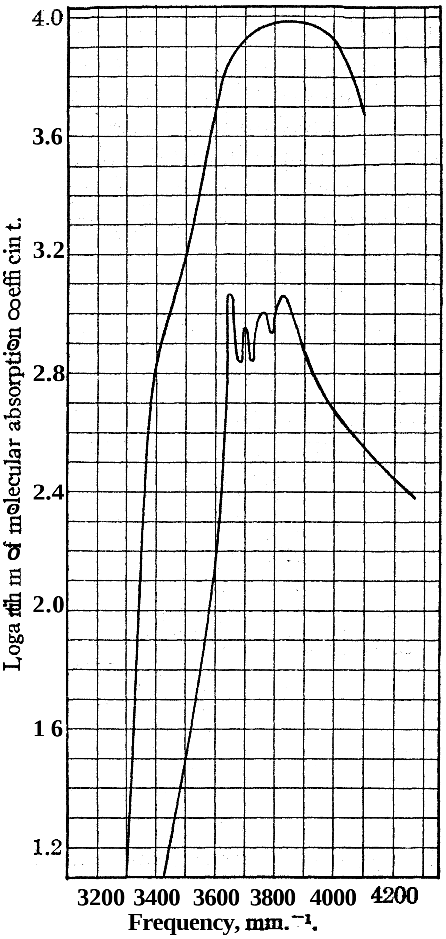


Fig. 1.—Upper curve, 1,1,3,3-tetraphenyl-1-butene; lower curve, 1,1,3-triphenyl-3-methylhydrindene.

An attempt was made to establish the identity of the red intermediate compound formed in the various reactions by means of absorption spectra in the visible region, using a Nutting photometer and a Hilger wave length spectrometer. The following solutions were investigated: (1) methyldiphenylcarbinol in concentrated sulfuric acid, (2) methyldiphenylchloromethane and stannic chloride in benzene, (3) diphenylethylene, stannic chloride and hydrochloric acid in benzene, and (4) tetraphenylbutene, stannic chloride and hydrochloric acid in benzene. All showed a rapid increase in absorption in the violet region and gave an indication of a band with its peak near the edge of the visible part of the spectrum. The location of this peak could not be definitely determined, due to the limitations of the apparatus at wave lengths below 4500 Å. Spectrographic measurements of the absorption spectra of these solutions are to be undertaken in order to obtain this information.

In many of our preliminary experiments mixtures of the unsaturated and saturated dimexs of diphenylethylene were obtained and it was desirable to determine the amount of each isomer present, but the separation by means of fractional crystallization was tedious and unsatisfactory. The mixtures did not melt sharply and did not crystallize readily on cooling, so that the melting point and solidification point were of no value for this purpose. The index of refraction of a concentrated solution of the material could not be used, due to the fact that the indices of refraction of the pure isomers were too nearly alike. The absorption curves of the two dimers are quite different though, as will be seen from Fig. 1, and therefore the composition of a mixture could be quite accurately determined from the molecular absorption coefficient at frequencies between 3425 and 3600. The absorption curves should also prove of value in establishing the structure of other indene derivatives which are not readily synthesized.

The measurements of the absorption spectra were made with a Judd-Lewis sector photometer and a Hilger quartz spectrograph, size C, by Dr. L. C. Anderson of this Laboratory, for whose assistance we wish to express our appreciation.

Experimental

Methyldiphenylchloromethane.—This compound was prepared by treating a benzene solution of the carbinol with dry hydrochloric acid gas at a temperature below 10° in the presence of anhydrous calcium chloride to remove the water formed in the reaction. Attempts to isolate the chloride by concentrating the solution gave a colorless oil which could not be crystallized, although an analysis for chlorine showed that no appreciable decomposition had taken place. A sample of the chloride was prepared in low-boiling petroleum ether, the solvent removed under reduced pressure at 0° and a stream of dry air passed through the residual oil to remove traces of hydrochloric acid. On analysis, 16.0% of chlorine was obtained, the calculated value being 16.4%. At room temperature the chloride decomposes slowly to give the ethylene and hydrochloric acid, a small amount of the unsaturated dimer of diphenylethylene being formed.[13]

1,1,3-Triphenyl-3-methylhydrindene.—Twenty-five grams of methyldiphenylcarbinol was dissolved in 250 cc. of benzene and converted into the chloride as described above. Ten grams of anhydrous stannic chloride was then added and the solution maintained below 10° for several hours, after which it was allowed to stand at room temperature. Upon the addition of the stannic chloride, the solution acquired a deep red color which gradually faded to a light brown. After one week it was washed thoroughly with water, dried and concentrated, and the residue dissolved in absolute alcohol. from which the triphenylmethylhydrindene was obtained in colorless crystals melting at 143'; yield, 95–97%. If the reaction is stopped after one day at room temperature. the yield is about 80%. An attempt to accelerate the reaction by heating on the steam-bath gave a decreased yield due to the formation of diphenylethylene and the unsaturated dimer.

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[13] Blicke and Powers, THIS JOURNAL, 51,3383 (1929).

Saturated Dimer of α-Methylstyrene.—This compound was prepared from dimethylphenylcarbinol by the method described above. The oily product from the concentration of the solution was rubbed with a small amount of alcohol, whereby a solid separated which was filtered and recrystallized. An additional amount of the product was obtained by distilling the oily residue and crystallizing the fraction which boiled at 128–135° at 3 mm. from alcohol. The combined yield of the dimer was 88% and the melting point 52°. The same compound is obtained if the stannic chloride used in the reaction is replaced by ferric chloride, aluminum chloride, antimony pentachloride or zinc chloride; stannic chloride and antimonic chloride have the advantage over the other reagents in that they are soluble in benzene. Staudinger and Breusch[14] have previously prepared this compound in 72% yield by the action of stannic chloride on α-methylstyrene.

Oxidation of 1,1,3-Triphenyl-3-methylhydrindene.—Five grams of the hydrocarbon was dissolved in 100 cc. of glacial acetic acid and 25 g. of chromic acid was cautiously added. The reaction was allowed to proceed rapidly with just enough cooling to prevent it from becoming violent, and was usually complete in about half an hour. After one hour the solution was poured into water, cooled to 0° with ice and partially neutralized by adding a solution of 50 g. of sodium hydroxide, which seemed to change the character of the precipitate so that it was easier to filter. The product was washed with water on the filter and air dried. No further material could be recovered from the filtrate by extraction with ether.

The crude oxidation products obtained from a number of runs were combined and extracted with hot water. From the water solution a small amount of oil was obtained by extraction with ether and evaporation of the solvent. Crystallization of the oil from alcohol gave a mixture of colorless, thin plates which after recrystallization melted at 95°, and colorless serrated tables which melted at 146°. A small amount of benzoic acid was obtained by sublimation of that portion of oil which failed to crystallize.

The residual oxidation product was then treated under rapid stirring with warm 25% sodium hydroxide solution and the mixture allowed to settle. The supernatant liquid was decanted or siphoned off and the operation repeated twice to insure removal of all of the alkali-soluble material. The product which was insoluble in alkali was steam distilled and the distillate extracted with ether. A small amount of oil was obtained from the ether solution which upon crystallization from alcohol gave the 146° compound along with long thin colorless needles which melted after recrystallization at 279°. The portion of oil which did not crystallize was treated with hydroxylamine hydrochloride and deposited benzophenone-oxime, which was identified by a mixed melting point. Extraction with ether of the non-volatile residue from the steam distillation, evaporation of the solvent and crystallization of the product from alcohol gave an additional quantity of the 146° compound.

The material soluble in 25% sodium hydroxide solution was precipitated with dilute hydrochloric acid, and the precipitate washed with water and air dried. The yield of this product was 40% of the weight of hydrocarbon oxidized. The material was stirred with a slight excess of dilute sodium hydroxide solution in which about 20% remained insoluble. This was filtered, washed with water, air dried and dissolved in alcohol. Two compounds were recovered from the solution, the 146° compound and large colorless needles which after recrystallization melted at 120°. The solution obtained by redissolving the oxidation product in dilute sodium hydroxide solution was treated with ether and the extracted material crystallized from alcohol. More of the 120° compound was obtained and also a small amount of small colorless needles which melted at 295° after recrystallization. The alkaline solution was then precipitated with dilute hydro-

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[14] Staudinger and Breusch, Ber., 62, 450 (1929).

chloric acid and the precipitate dissolved in alcohol. The solution deposited a considerable amount of colorless prisms melting at 225°. Since most of this product failed to crystallize, it was dissolved in excess of ammonium hydroxide, the solution diluted several times and then concentrated to its original volume on the hot-plate, when part of the material separated as an oil. The fraction which remained in solution was precipitated with dilute hydrochloric acid and the precipitate dissolved in ethyl alcohol, from which colorless needles were obtained which melted at 245° after recrystallization. The fraction which was precipitated was also dissolved in alcohol and gave very fine colorless needles which after recrystallization melted at 285°. The portion which did not crystallize was then dissolved in ether and extracted with 0.25 *N* ammonium hydroxide solution, The extracted material was precipitated from the ammoniacal solution by dilute hydrochloric acid and dissolved in alcohol from which a considerable quantity of colorless rhombohedral prisms melting at 190° was deposited. From the ether solution. more of the 285° compound was obtained.

The compounds melting at 95 and 295°, respectively, were not obtained in sufficient quantities for macro analysis. The analyses of the other compounds and the solubility in hot 5% sodium hydroxide solution and hot 5% ammonium hydroxide solution are given in Table I. It will be seen that in general the oxidation products which were isolated have a complex structure. Only traces of benzoic acid and benzophenone were obtained. The compound melting at 146° was identified as o-dibenzoylbenzene, and gave no depression in melting point when mixed with a sample of this compound prepared by the oxidation of *o*-dibenzylbenzene. The other compounds have not as yet been identified.

TABLE I

ANALYSES AND SOLUBILITY DATA OF THE OXIDATION PRODUCTS OF 1,1,3-TRIPHENYL-3-METHYLHYDRINDENE

M. p. of compound, °C. (uncorr.)	Soly. in hot 5% NaOH soln.	Soly. in hot 5% NH_4OH soln.	Formula	Calculated C, %	Calculated H, %	Found C, %	Found H, %
120	Insol.	Insol.	$C_{16}H_{12}O_2$	81.32	5.12	81.16	5.06
146	Insol.	Insol.	$C_{20}H_{14}O_2$	83.88	4.93	83.73	4.96
190	Sol.[a]	Sol.	$C_{23}H_{20}O_2$	84.10	6.14	83.99	6.19
225	Slightly[b]	Insol.	$C_{21}H_{14}O_3$	80.23	4.49	79.98	4.49
245[c]	Sol.	Sol.	$C_{24}H_{22}O_4$	76.97	5.93	76.92	6.89
279	Insol.	Insol.	$C_{22}H_{16}O_3$	80.45	4.92	80.47	4.89
285[d]	Sol.	Insol.	$C_{16}H_{12}O_2$	81.32	5.12	81.14	5.09

[a] The sodium salt is insoluble in concentrated NaOH solution. [b] Dissolves slowly in hot concentrated NaOH solution. [c] This compound may be α-methyl-α,γ,γ-triphenylglutaric acid. [d] The properties of this compound agree with those described for an anhydro derivative of β-benzoyl-α-phenylpropionic acid. Anschütz and Montfort, *Ann.*, 284, 5 (1895); Hann and Lapworth, J. *Chem. Soc.*, 85, 1362 (1904).

Polymerization of Asymmetrical Diphenylethylene.—Ten grams of the ethylene was dissolved in 75 cc. of benzene and treated with 4 g. of anhydrous stannic chloride at room temperature. The solution developed a light green color which faded to a light brown during the course of a day or two. After seven days at room temperature the solution was washed thoroughly with water, dried and concentrated. The product was diolved in alcohol, from which the unsaturated dimer, 1,1,3,3-tetraphenyl-1-butene was obtained in 77% yield, the residue being unchanged ethylene. Heating the reaction mixture on the steam-bath decreased the yield.

A similar reaction was carried out at room temperature using benzene which had been partially saturated with dry hydrochloric acid. The same light green color appeared initially, but after two hours the solution had become dark red, which color persisted for about a day and then faded to a light brown. Crystallization of the product from absolute alcohol gave a 90% yield of the saturated dimer, 1,1,3-triphenyl-3-methylhydrindene.

Rearrangement and Depolymerization of 1,1,3,3-Tetraphenyl-1-butene.—This compound in benzene solution is not rearranged under the influence of stannic chloride but is partially depolymerized. Five grams of the butene in 40 cc. of benzene was treated with 2 g. of stannic chloride, whereupon the solution acquired a light green color which persisted for about a day. After seven days at room temperature the solution was washed with water, dried and concentrated, and the product dissolved in alcohol, from which 80% of the butene was recovered. The residue was distilled in vacuum and gave 0.7 g. of asymmetrical diphenylethylene. No appreciable rearrangement was observed with stannic chloride in boilimg benzene, toluene or xylene, but when 5 g. of the butene was added to 50 cc. of stannic chloride and the solution refluxed for one week, a 90% yield of the saturated isomer was obtained.

The rearrangement is effected readily at room temperature provided hydrochloric acid is present. Five grams of the butene was dissolved in 40 cc. of benzene which was partially saturated with dry hydrochloric acid gas and 2 g. of stannic chloride was added. The solution first became light green and then dark red, the latter color fading after a day to a light brown. The solution was allowed to stand for a week at room temperature and was then washed with water, dried and concentrated. The residue was crystallized from absolute alcohol and gave a 90% yield of the saturated isomer, triphenylmethylhydrindene.

Summary

The saturated dimer of asymmetrical diphenylethylene has been identified as 1,1,3-triphenyl-3-methylhydrindene by means of its oxidation products.

The preparation of triphenylmethylhydrindene from methyldiphenylchloromethane has been described, and the method shown to be of general application.

The influence of stannic chloride on the polymerization of diphenylethylene and on the rearrangement and depolymerization of 1,1,3,3-tetraphenyl-1-butene has been described.

A reaction mechanism has been postulated for the formation of fluorene derivatives from triarylmethyl halides and for the formation of hydrindene derivatives from alkylarylmethyl halides.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO ORGANIC GERMANIUM DERIVATIVES. IV. DIPHENYL GERMANIUM AND OCTAPHENYL GERMANOPROPAEJE

BY CHARLES A. KRAUS AND CECIL L. BROWN

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I. Diphenyl Germanium

It might be expected that diphenyl germanium could be prepared by the reduction of diphenyl germanium dihalides. The reduction of the corresponding tin[1] derivatives is readily effected by means of the alkali metals in liquid ammonia. In the case of germanium, however, a corresponding reduction cannot be accomplished because of the tendency of the dihalides to ammonolyze. However, since diphenyl germanium dichloride is not ammonolyzed in ethylamine, it was thought that reduction might be effected by means of lithium in that solvent. Lithium is used in preference to sodium or potassium since it is readily soluble in ethylamine.

The reduction of diphenyl germanium dichloride in ethylamine proved impractical as will be shown below. Accordingly, the attempt was made to reduce it by means of metallic sodium in xylene. Morgan and Drew[d] have effected the reduction of the triphenyl germanium halide by this means. This method proved successful although the yields obtained were disappointingly low.

Action of Ethylamine upon Diphenyl Germanium Dichloride.—In a preceding article of this series it was shown that diphenyl germanium dichloride is completely ammonolyzed in liquid ammonia.[3] It was thought, however, that the chloride might be dissolved in ethylamine without ammonolysis. Accordingly, a weighed quantity of the dichloride was treated with ethylamine in a weighed reaction tube. On initial addition of the amine, a solid was formed which dissolved readily in an excess of the solvent. A similar result was obtained when ethylamine was passed through a solution of the dichloride in dry benzene. A precipitate was initially formed which dissolved on further addition of amine.

On removing the ethylamine after solution of the dichloride, a definite compound could not be isolated. At 90 to 100°, at low pressures, the dichloride began to distil to the colder parts of the tube, although all the amine had not been removed. The amount of amine left in the reaction product varied with the conditions of the experiment. In one instance 0.94 millimole of the dichloride retained 5.17 millimoles of amine at 20°

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[1] Kraus and Greer, This Journal, 47,2568 (1925).

[2] Morgan and Drew, J. *Chem. Soc.*, 127,1760 (1925).

[3] Kraus and Brown, This Journal, 52,3690 (1930).

and 38 mm. pressure. After pumping for one hour at 20°, 3.0 millimoles were retained and, after pumping for two hours at 100°, 0.43 millimole.

It was not possible to separate the initial solid in pure condition. On evaporating the solution, a liquid remained which retained amine with great tenacity and from which a solid could not be separated. The small quantity of amine retained at 100° indicates that ammonolysis does not take place.

Reduction of Diphenyl Germanium Dichloride in Ethylamine.—Since the dichloride does not ammonolyze in ethylamine, it was thought that it might be reduced to free diphenyl germanium by means of lithium in ethylamine solution. For this purpose, a weighed quantity of the dichloride was dissolved in ethylamine, cooled in a bath of liquid ammonia, and an equivalent quantity of lithium was added. The metal reacted readily with the dichloride, yielding a pale yellow solution. Only an insignificant quantity of hydrogen was evolved, which showed that the dichloride was not appreaably ammonolyzed. The solvent was evaporated and the two-legged tube was exhausted at a temperature of 100°, dry ether was condensed on the reaction product and the soluble materials were separated from the lithium chloride by decanting the supernatant liquid into the second leg of the reaction tube. After removing the ether, the tube was exhausted at 100° and finally at 200°. The product left in the second leg of the tube was a resinous material which could not be crystallized. Crystals of lithium chloride remained in the first leg.

It was hoped that reaction would occur according to the equation

$$(C_6H_5)_2GeCl_2 + 2Li = (C_6H_5)_2Ge + 2LiCl$$

In spite of the high temperature at which the tube was exhausted, the weight of the reaction tube and its contents indicated the presence of ethylamine. In four experiments the amount of ethylamine retained varied from 0.14 to 0.39 mole of amine per mole of dichloride. Analysis of the resinous product obtained in different reactions gave a germanium content varying from 29.2 to 31.2%. The germanium content of diphenyl germanium is 32.03%. It is evident that the product consisted largely of diphenyl germanium contaminated by some ethylamine and probably some other substances. It has since been found that certain of the metallo-organic free groups are capable of forming stable compounds with ethylamine. Thus Eatough[4] has shown that triphenyl silicon forms a compound $(C_6H_5)_3Si\cdot C_2H_5NH_2$. It is not improbable that ethylamine is retained in combination with the diphenyl germanium group and that the crystalline product cannot be obtained for this reason.

Reduction of Diphenyl Germanium Dichloride in Xylene.—Morgan and Drew[2] reduced triphenyl germanium halides by means of sodium in boiling xylene. It was thought that diphenyl germanium dichloride might be reduced according to the same method. The reduction was carried out in a 100-cc. flask with a long neck which was provided with a condenser jacket. An atmosphere of nitrogen was maintained in the flask throughout the process of reduction. The xylene used was digested with metallic sodium for a considerable period of time and was distilled directly into the reduction

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[4] Eatough, Thesis, Brown University, 1929.

flask under an atmosphere of nitrogen. Three grams of diphenyl germanium dichloride was added to 30 cc. of xylene, followed by thin slices of sodium freshly cut under xylene. The mixture was boiled for six hours and fresh sodium was added from time to time to insure the presence of a fresh metallic surface. As reduction proceeded, the solution took on a red color which gave way to yellow. At the end of the process, only a faint yellow color remained. The solution was rapidly decanted and filtered not and the brown residue left behind in the flask was washed several times with boiling xylene. On cooling the xylene solution, a small quantity of white crystals separated. These were thrown on a filter, while the filtrate was concentrated. Only a small quantity of crystalline material was obtained on further concentration. When the solvent was completely removed, a viscous yellow liquid remained which, on cooling, solidified to a resinous substance that could be chipped and ground to a powder. Attempts to crystallize this material from benzene, chloroform and xylene yielded only minute quantities of solid. The crystalline product amounted to from 10 to 20% of the theoretical yield. This was analyzed for germanium by the usual methods.

Anal. Subs., 0.1098, 0.0693: GeO_2, 0.0507, 0.0319. Calcd. for $(C_6H_5)_2Ge$: Ge, 32.03. Found: Ge, 32.05, 31.95; mean, 32.00,

The molecular weight of the crystalline product was determined in benzene by the boiling point method, using a modified Cottrell apparatus.

Mol. wt. Solvent, 13.18; solute, 0.5476, 0.7590; Δt 0.123, 0.170°; mol. wt. found, 902, 904; mean, 903.

The molecular weight of diphenyl germanium is 226.7. If four molecules of diphenyl germanium were polymerized, the molecular weight would be 907, which value is in close agreement with that found.

Properties of Diphenyl Germanium.—The crystalline material is readily soluble in benzene so long as the original yellow resin is present but, once separated from this resin, it is only slightly soluble in cold benzene, toluene or chloroform. Its solubility in hot solvents is limited and it is insoluble in petroleum ether. On slow crystallization from benzene, fine white crystals were obtained melting at 294–295° (corr.). These crystals undergo no change on exposure to the atmosphere.

The Resinous Reduction Product.—Analyses of the resinous material varied, depending upon the sample. The germanium content was found to range from 29.6 to 30.4% as against 32.03% for pure diphenyl germanium. The molecular weight of the resinous material, as determined in benzene by the cryoscopic method, was found to be 900 and 930 in two determinations, respectively.

The analyses and the molecular weight determinations indicate that the resin is an impure polymer. In many respects it resembles the product of reduction in ethylamine. No crystals could be obtained from this resinous material although numerous solvents were tried under varying conditions.

Disodium Diphenyl Germanide.—Disodium diphenyl germanide is readily prepared by treating diphenyl germanium with an equivalent quantity of sodium in liquid ammonia. For this purpose a reaction tube is used of the type outlined in the accompanying figure. The diphenyl germanium is introduced into the reaction tube A. The top of this tube is provided with a ground joint B which carries a stirring tube C that reaches to the bottom of the reaction tube. The stirring tube is provided with a stopcock D. The neck of the reaction tube is provided with a second stopcock E. The tubes F and G are connected with the system by means of de Khotinsky cement. The system makes connection with a source of pure ammonia, a manometer. a vacuum pump and with an adjustable mercury trap. The reaction tube is provided with a side arm J which carries a tube K, the end of which projects into the side arm and is fitted to J by means of a ground joint L. The sodium which is to be used in reducing the diphenyl germanium is weighed out under Nujol, washed with petroleum ether and introduced into tube K, which is then inserted into the ground joint. The reaction tube is then evacuated.

The reaction tube A is now surrounded by a bath of boiling ammonia and ammonia vapor is introduced through the stopcock D under a pressure about 20 cm. above that of the atmosphere. This pressure is regulated by the height of mercury in the mercury trap. When a sufficient quantity of ammonia has been condensed in the reaction tube, stopcock E is closed and, by turning the tube K about its axis in the ground joint, sodium is introduced into the reaction tube piece by piece.

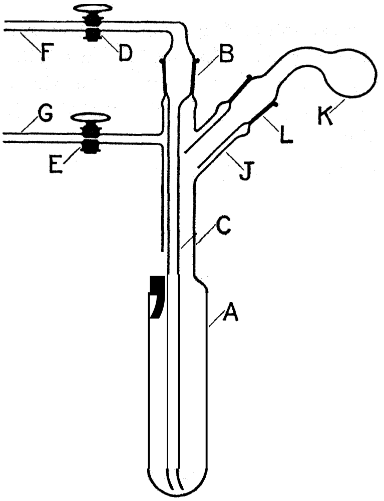

Fig. 1.—Reaction tube.

The sodium goes into a solution and reacts readily with the diphenyl germanium. The blue color, characteristic of the free metal, disappears and a yellow color replaces it. The reaction takes place in two steps, in which respect it resembles the corresponding reaction of dimethyl tin described by Kraus and Greer.[1] On the initial addition of sodium, the solution exhibits a yellow color and, when approximately one-half the equivalent amount of sodium has been added, the diphenyl germanium has been completely dissolved. This stage of the process corresponds to the formation of disodium tetraphenyl germanoethane. On further addition of sodium, the germanium bond is broken and disodium diphenyl germanide is formed. The latter compound is also soluble in liquid ammonia and imparts a deep red color to the solution. At higher concentrations the solutions are almost opaque.

Attempts were made to prepare a diphenyl germane by treating the solution of disodium diphenyl germanide with ammonium bromide. While in certain experiments evidence was found that the dihydride may have been formed initially, the compound could not be isolated. Seemingly, hydrogen is lost and more complex derivatives are formed. The final product was in all cases a viscous liquid.

II. Octaphenyl Germanopropane

Octaphenyl germanopropane could doubtless be prepared by treating disodium diphenyl germanide with triphenyl germanium halide in ammonia or other solvents. However, in view of the difficulty of preparing diphenyl germanium, it seemed preferable to prepare the germanopropane by treating sodium triphenyl germanide with diphenyl germanium dihalide in a suitable solvent. Reaction takes place according to the equation

$$2(C_6H_5)_3GeNa + (C_6H_5)_2GeCl_2 = 2NaCl + (C_6H_5)_8Ge_3$$

Preparation.—Sodium triphenyl germanide was prepared by adding 0.1437 g. (5.876 m. atoms) of sodium to 1.779 g. (2.93 m. moles) of hexaphenyl germano-ethane in liquid ammonia. The ammonia was allowed to evaporate and the tube containing the product was evacuated for twelve hours. The yellow color of the sodium salt gave way to white as the residual ammonia was removed. Dry benzene was then distilled onto the sodium triphenyl germanide, the tube was filled with nitrogen and 0.873 g. (2.93 m. moles) of diphenyl germanium dichloride was added. The reaction mixture was heated with occasional shaking for eight hours. The contents of the tube were then rapidly filtered and most of the solvent was removed by distillation. On cooling. a small crop of crystals appeared. These were separated by filtration and, by their melting point, identified as hexaphenyl germano-ethane. On further concentration of the filtrate, a second crop of crystals was obtained in the form of large flakes. These were removed, washed with cold chloroform and recrystallized from that solvent prior to analysis. On further evaporation of the original solution, a viscous liquid was left behind.

Anal. Subs., **0.1354,** 0.2023: GeO_2, **0.0506, 0.0762.** Calcd. for $Ge_3(C_6H_5)_8$: Ge. **26.11.** Found: Ge, 25.94, 26.14; mean, 26.04.

The molecular weight of the germanopropane was determined in benzene by the boiling point method.

Mol. wt. Solvent, **16.05, 15.67;** solute, **0.7071, 0.9811;** *At,* 0.135°, 0.195°; **mol. wt.** found, **871,875;** mean, **864;** calcd. for $Ge_3(C_6H_5)_8$: 834.

Properties.—Octaphenyl germanopropane is stable toward air and moisture. On rapid crystallization from chloroform, a fine white crystalline powder is obtained, while on slow crystallization plate-like crystals are formed. The compound is readily soluble in warm benzene and chloroform. It melts at 247–248° (corr.).

Action of Bromine on **Octaphenyl Germanopropane.**—As a further check on the structure of the germanopropane and in order to test the resistance of the Ge–Ge bond toward bromine, the compound was treated with bromine in carbon tetrachloride. Reaction took place at ordinary temperatures, the intensity of the color due to bromine gradually diminishing until, at the end of eighteen hours, the solution was but faintly yellow. This color disappeared entirely on warming the solution. On evaporation of the solvent, a crystalline mass resulted in which traces of a viscous liquid were present. The reaction product was extracted with petroleum ether and upon evaporation crystals were obtained that melted at 138°. This corresponds to the melting point of triphenyl germanium bromide. A small quantity of a viscous liquid was also obtained and, when this was treated with a drop of water, a white film was formed. This is characteristic of diphenyl germanium dibromide, the white film being due to the oxide formed on hydrolysis. The remainder of the crystalline product was unchanged octaphenyl germanopropane. It is evident that the Ge–Ge bond is less stable toward bromine than is the phenyl germanium bond. On bromination in carbon tetrachloride, the Ge–Ge linkage is broken down.

Summary

Diphenyl germanium dichloride is not ammonolyzed in ethylamine. The reduction of diphenyl germanium dihalide by means of lithium in ethylamine proved unsuccessful. The reduction product was a resinous material whose composition approximated that of diphenyl germanium but which could not be purified.

Diphenyl germanium, in crystalline form, was obtained by the reduction of diphenyl germanium dichloride by means of sodium in xylene. The yields were small, the greater proportion of the product consisting of a resinous material resembling that obtained on reduction in ethylamine.

Disodium diphenyl germanide was prepared by the action of sodium on diphenyl germanium in liquid ammonia.

Octaphenyl germanopropane was prepared by the action of sodium triphenyl germanide on diphenyl germanium dichloride in benzene solution.

PROVIDENCE, RHODE ISLAND

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

THE CLEAVAGE OF CERTAIN UNSYMMETRICAL 193-DIKETONES

BY WALTER M. KUTZ AND HOMER ADKINS

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A diketone of the type $R'C(O)CR_2C(O)R''$ may undergo alcoholysis to form either the ester $R'COOEt$ or $R''COOEt$, together with the corresponding ketones. Bradley and Robinson[1] found in the case of 18 out of 20 aryl 1,3-diketones that alkaline hydrolysis took place in such a way that the stronger of the two possible acids was produced in the larger amount. It was shown in a previous paper[2] that acetylbenzoylmethane and benzylacetylbenzoylmethane underwent alcoholysis in the presence of hydrogen chloride to give ethyl acetate unmixed with any ethyl benzoate. Having these facts in mind, the alcoholysis and hydrolysis of certain unsymmetrical 1,3-diketones were carried out with the view to ascertain to what extent structural factors and experimental conditions determine the point of cleavage. The ratios of products in the hydrolysis and alcoholysis of the following list of 1,3-diketones have been determined

$CH_3C(O)CH_2C(O)C_4H_9$-*n*
$CH_3C(O)CH_2C(O)C_5H_{11}$-*n*
$CH_3C(O)CH_2C(O)C_5H_{11}$-*iso*
$CH_3C(O)CH_2C(O)C_5H_{11}$-*sec.*
$CH_3C(O)CH_2C(O)C_5H_{11}$-*tert.*
$CH_3C(O)CH_2C(O)C_6H_5$(phenyl)
$CH_3C(O)CH(CH_2C_6H_5)C(O)C_6H_5$(phenyl)
$CH_3C(O)CH_2C(O)C_6H_{11}$(cyclohexyl)
$CH_3C(O)CH_2C(O)C_4H_3O$(furyl)

Alcoholysis was carried out by placing the desired amount of diketone, together with a one-half molar ratio of hydrogen chloride in ethanol, in a thermostat at 60° for four days. The volume of the alcoholysis mixture was approximately 25 ml. per 0.01 mole of diketone. Two ml. of phenylhydrazine per 0.01 mole of sample was then added to combine with the hydrogen chloride and ketones. After standing for two hours, the reaction mixture was distilled from an oil-bath at a temperature of 110–120°. At this stage the reaction mixtures from the five aliphatic diketones were treated with four successive portions (15 ml.) of butanol, each portion being distilled out under a pressure of 100 mm. before the addition of the next. This procedure was necessary in order to distil out the esters of the various butyric and valeric acids. The ester in the distillate was saponified with 0.1 N sodium hydroxide and the excess back titrated with sulfuric acid of the same concentration, phenolphthalein being used as an indicator. The mixture was evaporated to dryness and an amount of 0.3 N sulfuric acid, equivalent to the sodium salts of the fatty acids present, added. This solution was diluted with water until 50 ml. contained approximately 7.5 millimoles of acid.

In the case of four of the diketones, one of the esters which could be formed was too high boiling to be conveniently distilled out in the presence of phenylhydrazine. After completion of alcoholysis, the mixture was divided into two equal portions. To one phenylhydrazine was added and the ethyl acetate present distilled out with ethanol. The other half was analyzed for acetone by the sodium sulfite method as previously

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[1] Bradley and Robinson, J. *Chem. Soc.*, 129, 2356 (1926).

[2] Adkins, Kutz and Coffman, THIS JOURNAL, 52,3212 (1930).

described.[3] The alcoholysis sample was distilled, giving a distillate which contained ethyl acetate, ethanol, hydrogen chloride and any acetone; aqueous sodium hydroxide was then added to neutralize the acid and to saponify the ester. This mixture was distilled, any acetone present being thus obtained in an ethanol–water solution.

The method of analysis for the ratio of acids (or esters) produced in the cleavage of the diketones involved the partition of the acids between water and benzene, the titration of each layer with standard alkali and the calculation of the ratios of the acids present from the result of this titration and a knowledge of the partition of the acids involved between water and benzene.

Behrens[4] described the determination of a number of acids by the partition between ether and water. The greater insolubility in each other of benzene and water and the greater differences in the partition coefficients of the aliphatic acids for this pair of solvents[5] indicated that benzene was to be preferred to ether as the organic solvent.[6]

The results of the determination of the partition of the various acids (except acetic) at various concentrations between equal volumes of benzene and water is shown in Fig. 1. The concentration of acetic acid in the benzene layer was found to be from 1.9 to 2.2 millimoles per liter when the concentration in the water layer was from 75 to 110 millimoles per liter. In the later calculations the concentration of acetic acid in the benzene layer was taken as 2 millimoles per liter. Since all of the samples to be analyzed contained approximately 1.5×10^{-1} moles of sodium sulfate per liter, that concentration of the salt was always present in the water layer during the determination of the partition of the acids. The titrations were made on 25-ml. samples with 0.1 N sodium hydroxide, using phenolphthalein as an indicator, after partition had taken place over a two-hour period, the samples being shaken frequently while they were held in a thermostat at 25°.

The acid solutions obtained by the alcoholysis and hydrolysis of the various diketones were analyzed for the two acids present. Fifty ml. of the solution prepared as described above was placed in a separatory funnel and shaken with 50 ml. of benzene. After shaking for a few minutes it was placed in a thermostat at 25° and shaken at intervals of fifteen minutes over a period of two hours. The layers were separated and titrated with carbonate-free 0.1 N sodium hydroxide. From the previously determined partition ratios the amount of each acid present and consequently the amount of split was calculated. Using the data which were found in the analysis for the acids formed in the hydrolysis of acetylbutyrylmethane, a calculation of the percentage of acetyl split as compared to the total amount of hydrolysis is shown below. After partition of the aqueous acid solution with benzene, 63.0 ml. of 0.1 *N* alkali was required to neutralize 50 ml. of the water layer and 18.5 ml. of 0.1 N alkali for the same volume of the benzene layer. Therefore the amount of acid in the water layer was 6.3 millimoles and in the benzene layer 1.85 millimoles. The concentration of acetic acid in the benzene layer under the conditions used here had been determined to be approximately 2.0

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[3] Child and Adkins, THIS JOURNAL, 45, 3013 (1923).

[4] Behrens, *Z. anal. Chem.*, *69*, 97 (1926).

[5] Brown and Bury, *J. Chem. Soc.*, 123, 2430 (1923); Smith and White, *J. Phys. Chem.*, 33, 1953 (1929).

[6] *Cf.* Werkman, *Ind. Eng. Chem., Anal. Ed.*, 2, 302 (1930).

millimoles per liter or 0.1 millimole in 50 ml. of solution. The concentration of butyric acid in the benzene layer was accordingly 35 millimoles per liter. From the graph on which the partition data for the various acids had been plotted, the corresponding concentration of the butyric acid in the water layer was shown to be 48 millimoles per liter or 2.4 millimoles in 50 ml. The total amount of acetic acid was equal to the amount of acid in the water layer plus the amount of acetic acid in the benzene layer minus the amount of butyric acid in the water layer, i. e., 6.3 + 0.1 – 2.4 = 4.0 millimoles. The amount of butyric acid was determined by difference, the total acidity of the water and benzene layers less the amount of acetic acid, *i.* e., 8.15 – 4.0 = 4.15 millimoles. The percentage of "acetyl" cleavage was therefore 49% (4.0/8.15 × 100).

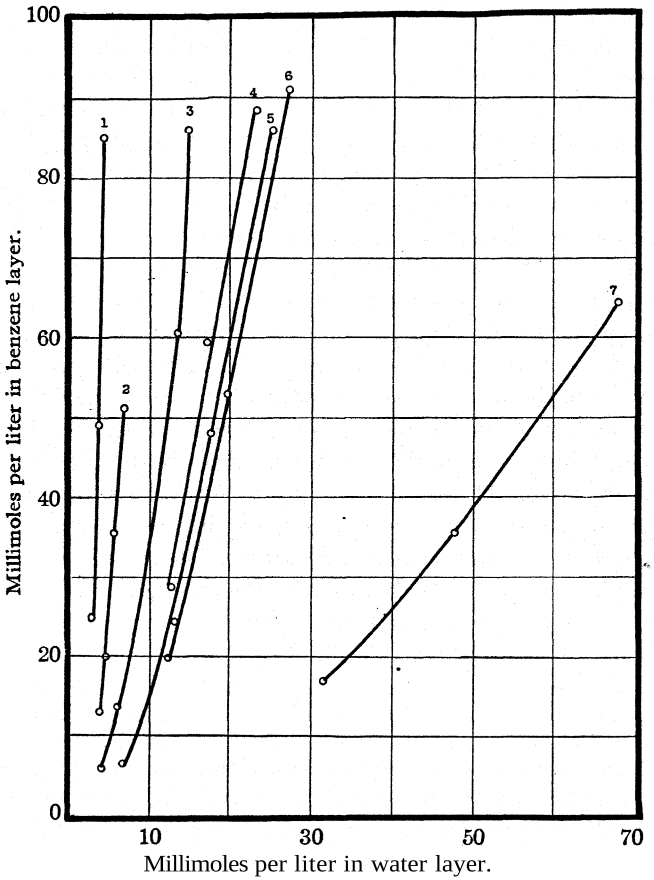

Fig. 1.—Distribution of (1) cyclohexanoic, (2) benzoic, (3) trimethylacetic, (4) *n*-valeric, (5) methylethylacetic, (6) isovaleric, and (7) a-butyric acids at various concentrations between equal volumes of benzene and water containing 0.15 mole of sodium sulfate per liter.

The accuracy of the method of analysis was tested by the analysis of mixtures of known composition of acetic and butyric acids, of acetic and valeric acids, of ethyl acetate and ethyl butyrate, and of ethyl acetate and ethyl valerate. The results were as follows. A solution containing the acids in the ratio 51.5% acetic acid and 49.5% butyric acid was found to contain 50 and 50% acetic acid in two analyses. A solution containing 52.4% acetic and 47.6% valeric acids showed by analysis 53 and 53% acetic acid. A mixture of esters containing 49.8% ethyl acetate and 50.2% ethyl butyrate showed 47 and 46% acetic acid upon analysis. A mixture of ethyl acetate (56.7%) and ethyl valerate (43.3%) showed 55% acetic acid after saponification and partition. Another sample containing 74.9% of ethyl acetate showed by analysis 77%.

The determination of the products formed in hydrolysis was very similar to the method just described. The diketone was placed in a thermostat at 60° with an excess of 0.1 N sodium hydroxide. Twenty-four hours were sufficient to give practically complete hydrolysis, except in the case of acetyltrimethylacetylmethane, which required at least twice that length of time. The hydrolysis sample was back titrated with standard sulfuric acid and then evaporated to dryness. The procedure from this point on was the same as for the alcoholysis samples, *i. e.*, the addition of a calculated quantity of standard sulfuric acid, partition, titration and calculation.

In the hydrolysis of acetylbenzoylmethane, benzylacetylbenzoylmethane, acetylcyclohexoylmethane and acetylfuroylmethane, one of the acids which could be formed is only slightly soluble in water at 25°, so in these cases the whole of an hydrolysis sample was subjected to partition rather than an aliquot portion. The aqueous acid solution was not homogeneous and a representative sample could not be secured.

The amounts of acids, expressed in millimoles, from the esters formed in the alcoholysis of five diketones are given below: from acetylbutyrylmethane, acetic acid 4.15 and 4.30, butyric acid 5.47 and 5.35; from acetylvalerylmethane, acetic acid 6.26 and 5.53, valeric acid 4.06 and 3.37; from acetylisovalerylmethane, acetic acid 4.04 and 5.25. isovaleric acid 2.55 and 2.75; from acetyl-*sec.*-valerylmethane, acetic acid 5.80 and 5.90, *sec.*-valeric acid 1.38 and 1.38; from acetyltrimethylacetylmethane, acetic acid 6.04, 6.14 and 6.44, trimethylacetic acid 0.56, 0.56 and 0.80.

The amounts of ethyl acetate and acetone expressed in millimoles formed in the alcoholysis of four diketones (which might split to give high-boiling esters) are given below: from acetylbenzoylmethane, ethyl acetate 8.66 and 8.66, acetone, none; from acetylcyclohexanoylmethane, ethyl acetate 5.80 and 6.02, acetone 4.3 and 4.0; from benzylacetylbenzoylmethane, ethyl acetate 7.70 and 8.30, ethyl benzoate, none; from acetylfuroylmethane, ethyl acetate 13.1 and 12.4, acetone, none.

The amounts of acids, expressed in millimoles, from the alkaline hydrolysis of nine diketones are given below: from acetylbutyrylmethane, acetic acid 4.00 and 4.04, butyric acid 4.15 and 4.15; from acetylvalerylmethane, acetic acid 4.38 and 4.42, valeric acid 3.58 and 3.66; from acetylisovalerylmethane, acetic acid 5.52 and 5.80, isovaleric acid 271 and 2.87; from acetyl-*sec.*-valerylmethane, acetic acid 4.85 and 4.90, *sec.*-valeric acid 2.95 and 2.95; from acetyltrimethylacetylmethane, acetic acid 4.25, 4.35 and 4.93, trimethylacetic acid 3.15, 3.15 and 3.35; from acetylbenzoylmethane, acetic acid 5.09 and 5.67, benzoic acid 0.82 and 0.93. From acetylcyclohexanoylmethane, acetic acid 4.69 and 4.74, cyclohexanoic acid 3.71 and 3.76; from benzylacetylbenzoylmethane, acetic acid 5.25 and 5.90, benzoic acid 2.35 and 2.70; from acetylfuroylmethane, acetic acid 8.62 and 8.78, furoic acid, none.

There is given in Table I a summary calculated from the above data which indicates the extent to which the linkage on the one side or the other of the "methane" carbon atom was split by alcoholysis or hydrolysis.

There does not appear to be a close agreement between the strength of the acids and the ratio in which they were produced through hydrolysis,

TABLE I

THE RATIO OF PRODUCTS IN THE CLEAVAGE OF CERTAIN 1,3-DIKETONES

Diketone	Alcoholysis		Hydrolysis	
	$CH_3\text{—}\underset{\vert}{C}\text{=}O$, %	$R\text{—}\underset{\vert}{C}\text{=}O$, %	$CH_3\text{—}\underset{\vert}{C}\text{=}O$, %	$R\text{—}\underset{\vert}{C}\text{=}O$, %
Acetylbutyrylmethane	43.5	56.5	49	51
Acetylvalerylmethane	61	39	55	45
Acetylisovalerylmethane	65.5	34.5	67	33
Acetyl-*sec.*-valerylmethane	81	19	62	38
Acetyltrimethylacetylmethane	91	9	58	42
Acetylbenzoylmethane	100	0	86	14
Acetylcyclohexanoylmethane	58.5	41.5	56	44
Benzylacetylbenzoylmethane	100	0	69	31
Acetylfuroylmethane	100	0	100	0

although in the case of the hydrolysis of four of the five aliphatic diketones the stronger acid was produced in the larger amount. Furoic acid is forty times as strong as acetic acid, yet none was produced in the hydrolysis of acetylfuroylmethane. Benzoic acid is three to four times stronger than acetic acid yet over five times as much acetic as benzoic acid was produced in the hydrolysis of acetylbenzoylmethane, while when one of the hydrogens on the "methane" carbon atom had been replaced by a benzyl group the ratio of acetic to benzoic acid was slightly more than 2 to 1. Butyric and acetic acids were produced in almost equal amounts by the hydrolysis of acetylbutyrylmethane, while twice as much acetic acid as isovaleric acid was produced in the hydrolysis of acetylisovalerylmethane despite the fact that isovaleric acid is stronger than butyric acid.

In the case of three of the nine diketones (acetylisovalerylmethane, acetylcyclohexanoylmethane and acetylfuroylmethane) there was no essential difference between the ratio of the products produced in hydrolysis and alcoholysis. In one case (acetylbutyrylmethane) the cleavage to produce an acetyl compound was slightly less in alcohol than in water, but in this determination (acetic and butyric acids) the experimental error was largest. In the other five cases there was from 10 to 45% greater production of the acetyl compound in acid alcoholysis than in alkaline hydrolysis. In general it would seem that the ratio of products is less modified by changes in structure in the case of alkaline hydrolysis than in acid alcoholysis.

The data for the four diketones which have a butyl group at one end of the diketone molecule show clearly that increased branching in the radical greatly slows up the rate of alcoholysis (both actually and relatively) at that side of the molecule. The diketone having the n-butyl group breaks to give 39% of the five-carbon acid, the diketone having the isobutyl group gives 34.5% of the corresponding acid, the *sec.*-butyl group gives 19% of the acid while with the *tert.*-butyl group the production of the five-carbon acid has dropped to 9%. In contrast with this is the fact that the alkaline hydrolysis was but little affected by these changes in structure. In this connection it should be pointed out that the alcoholysis of the diketones containing the *sec.*-butyl and *tert.*-butyl groups was very slow and did not go more than 20 to 30% to completion in 150 hours, while in the case of all the other diketones (except benzylacetylbenzoylmethane) alcoholysis was 100% in less than 100 hours. These facts might be explained on the basis of steric hindrance were it not for the fact that the unsaturated cyclic radicals phenyl and furyl decreased alcoholysis on that side of the diketone to the vanishing point while the cyclohexyl radical permitted a 41.5% cleavage to form ethyl cyclohexanoate. It appears then that the factors which are operating in these cases to determine the point of cleavage are probably constitutional rather than steric.

It has been pointed out[2] that there is a correlation between the extent of enolization of a diketone and the rate of alcoholysis in the presence of hydrogen chloride. Thus it is possible that the ratio of the products in the acid alcoholysis of an unsymmetrical diketone represents approximately the ratio of the extent of the enolization of the two carbonyl groups.

The authors wish to emphasize that in their opinion the ratios of products formed in the solvolysis of the 1,3-diketones as reported in this paper are simply a measure of the relative rates of two competitive reactions and are in no sense measures of the strength or thermodynamic stability of the linkages involved. As noted in another paper they have so far failed in all attempts to determine the latter values for any 1,3-diketones. Such values are as much a characteristic of a given structure as its absorption spectra, while the ratio of the rates of two alternative modes of reaction are modifiable almost without limit. It is interesting to note that the experimental work reported in this paper shows that increased branching in the butyl radical decreases the rate of cleavage of the acyl radical containing it from the remainder of the molecule to which it is attached, while Conant, Small and Sloan[7] have shown that increased branching in the butyl group increases the extent of dissociation of hexasubstituted ethanes. This latter determination is, of course, a measurement of the thermodynamic stability of the carbon to carbon linkage.

Preparation and Purity of Reagents.—Acetylbutyrylmethane, acetylvalerylmethane, acetylisovalerylmethane, acetyl-*sec.*-valerylmethane, acetyltrimethylacetylmethane, acetylbenzoylmethane and acetylcyclohexanolmethane were prepared by the method previously described,''. e., by condensing ethyl acetate with the proper methyl ketone in the presence of metallic sodium. Acetylfuroylmethane was prepared by condensing ethyl furoate with acetone in the presence of sodium ethoxide, the method being the same as for diacetylmethane, except that toluene was substituted for the excess ester used as a solvent in that preparation. The preparation of benzylacetylbenzoylmethane was described in the previous paper. There is given below a summary showing the physical constants, yields and analyses where necessary of the various reagents used in this investigation. Acetylbutyrylmethane: yield 48%, b. p. 173–175°, d_{25}^{25} 0.9375

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[7] Conant, Small and Sloan, THIS JOURNAL, 47, 3068 (1925); 48, 1743 (1926).

[Morgan and Drew, *J. Chem. Soc.*, 125,737 (1924)]; **acetylvalerylmethane:** yield 58%, b. p. 64–66° (5 mm.), d_{25}^{25} 0.9218 [Morgan and Holmes, *ibid.*, 760 (1924)]; **acetyl-*sec.*-valerylmethane:** yield 52%, b. p. 62–65° (5mm.), d_{25}^{25} 0.9160 [Anal. Calcd. for $C_8H_{14}O_2$: C, 67.55%; H, 9.93%. Found: C, 67.32, 67.26%; H, 9.77, 9.62%]; acetyltrimethylacetylmethane: yield 51%, b. p. 164–167°, d_{25}^{25} 0.9155 [Couturier, *Compt. rend.*, 150, 928 (1910)]; acetylbenzoylmethane: m. p. 57–58' (see earlier paper); benzylacetylbenzoylmethane:, m. p. 55–56° (see earlier paper); **acetylcyclohexanoylmethane:** yield 55%, b. p. 104–107° (10 mm.), d_{25}^{25} 1.0080 [Godchot, *Compt. rend.*, 151, 1131 (1910)]; acetylfuroylmethane: yield 20%, m. p. (from ethanol and water), 30–31° [Anal. Calcd. for $C_8H_8O_3$: C, 63.13%; H, 5.30%. Found: C, 62.98, 62.80%; H, 5.41, 5.38%]; acetic acid: b. p. 116–117° (after crystallization); butyric acid: b. p. 161–161.5°; valeric acid: b. p. 180–182°; isovalenc acid: b. p. 172–174'; methylethylacetic acid: b. p. 172–174°; trimethylacetic acid: m. p. 34–35°; benzoic acid: m. p. 120–121°; cyclohexanoic acid: m. p. 28–30'.

Summary

The ratio of esters and of salts of acids produced in the acid alcoholysis and the alkaline hydrolysis, respectively, of nine unsymmetrical 1,3-diketones has been determined and the results summarized in tabular form. There was not found to be a close correlation between the amounts and the strength of the acids produced in hydrolysis such as had previously been observed in the case of certain diaryl 1,3-diketones. The ratio of products was less modified by changes in structure in the case of alkaline hydrolysis than in acid alcoholysis. Increased branching in the radical at one end of the diketone molecule decreased the cleavage on that side but this does not appear to be due entirely to steric effects, for the cyclohexyl group was much less effective in this regard than the phenyl or furyl radical. It has been suggested that the ratio of products is a measure of the relative extent of enolization of the two carbonyl groups in these unsymmetrical diketones.

The preparation of acetyl-*sec.*-valerylmethane and acetylfuroylmethane is reported for the first time.

MADISON, WISCONSIN

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

STUDIES OF CONJUGATED SYSTEMS. V. THE PREPARATION AND CHLORINATION OF BUTADIENE

BY IRVING E. MUSKAT AND HERBERT E. NORTHRUP

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The addition reactions of conjugated systems have been for some time the subject of an investigation in this Laboratory.[1] In our earlier work we were mainly concerned with the addition reactions of a-substituted conjugated compounds, $RCH{=}CHCH{=}CH_2$, but in order to ascertain the effect of conjugation, free from the influence of substituent groups, we undertook an investigation of the addition reactions of butadiene, $CH_2{=}CHCH{=}CH_2$. The present paper contains the results of a study of the preparation and chlorination of butadiene.

The preparation of butadiene was first reported by Caventou,[2] who obtained it by passing the vapors of fusel oil through a hot tube. Since then it has been found in varying amounts (usually very small) in the pyrogenic decompositions of a large number of organic compounds. The possibility of using butadiene as a raw material for the production of rubber stimulated a great deal of work on the preparation of this hydrocarbon. Harries,[3] one of the pioneers of rubber chemistry, has shown that while excellent rubber is obtained by the polymerization of isoprene, rubber of still better quality is produced by the polymerization of butadiene. Most of the methods that have been patented for the preparation of butadiene are based on the pyrogenic decomposition and cracking of different petroleum products.[4] However, the yields of butadiene obtained by these methods invariably have been low.

A different method for the preparation of butadiene was suggested by Perkin[5] based on the method he developed for the preparation of isoprene. This method may be formulated as follows

$$\underset{\text{Butyl alcohol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow{\text{Dry HCl}} \underset{\text{Butyl chloride}}{CH_3CH_2CH_2CH_2Cl}$$

$$\text{Butyl chloride} \xrightarrow{Cl_2} \underset{\text{butane dichlorides}}{\text{Mixture of } \alpha,\beta\text{-}, \alpha,\gamma\text{- and } \alpha,\delta\text{-}}$$

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[1] Muskat and Huggins, THIS JOURNAL, 51, 2496 (1929); Muskat, Becker and Lowenstein, *ibid.*, 52, 326 (1930); Muskat and Becker, *ibid.*, 52, 812 (1930); Muskat and Grimsley, *ibid.*, 52, 1574 (1930).

[2] Caventou, Ann., 127, 348 (1863).

[3] Harries, *ibid.*, 383, 213 (1911).

[4] Brooks. "Chemistry of Non-Benzenoid Hydrocarbons," The Chemical Catalog Co., Inc., New York, 1922, gives a rather complete review of the various methods that have been used for the preparation of butadiene.

[5] Perkin, J. *Soc.* Chem. Ind., 31, 616 (1912).

$$\text{Butane dichlorides} \xrightarrow[\text{at } 470^\circ]{\text{Soda lime}} \underset{\text{Butadiene}}{CH_2{=}CHCH{=}CH_2}$$

He states that he tried this method once and that the yield appeared to be good, but he gave no actual figures.

Since this 1912 paper Perkin has not published further concerning the preparation of butadiene or the development of the process he suggested. It is also of interest that of the many research investigations published since 1912 in which butadiene was used, not any of the investigators prepared the butadiene according to the method suggested by Perkin. We must, therefore, conclude that the method of preparing butadiene devised by Perkin was not considered successful.

Since we intended to make an extended study of butadiene and its addition reactions we made a preliminary investigation of the various methods suggested for its preparation. The method devised by Perkin appeared the most promising and we have developed this method so that it gives a much better yield of butadiene than that obtained by any of the other methods.

n-Butyl alcohol was converted into n-butyl chloride according to the method of Norris[6] by heating the alcohol with concentrated hydrochloric acid and anhydrous zinc chloride. The pure chloride was then further chlorinated to the dichloride. In order to insure the complete conversion, as far as possible, of the monochloride to the dichloride without the formation of any higher chlorinated products, a specially designed apparatus was used. This was modeled after a similar apparatus used by Perkin in his work on the chlorination of isoamyl chloride. A detailed description of the apparatus will follow in the Experimental Part. It was possible to chlorinate in this apparatus two liters of butyl chloride to the dichloride in about six hours.

The chlorinated reaction mixture was then distilled through a fractionating column. From the distillation temperatures of the fractions collected it appeared that the chlorinated product consisted of a mixture of some unreacted butyl chloride and the α,β-, α,γ- and α,δ-dichlorobutanes (possibly also some α,α-dichlorobutane). Detailed data concerning the yields of these fractions will be found in the Experimental Part.

Each of the fractions of the dichlorobutanes was distilled over coarse soda lime contained in an iron tube heated at a temperature of about 700–730°. The volatile products coming from the hot tube were passed through several condensers and wash bottles and finally absorbed in chloroform or ligroin to be treated as desired. A diagram of this cracking apparatus is included in the Experimental Part with the yields of butadiene obtained from each fraction of the dichlorobutane mixture. The best yield was obtained from the α,γ-dichlorobutane, which was about 30 mole per cent. of the theoreti-

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[6] Norris, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 27.

cal. This is considerably higher than the yield of butadiene reported from other methods,

The addition of bromine to butadiene was first studied by Griner,[7] then by Thiele[8] and more recently by Farmer and his students.[9] The latter have definitely shown that butadiene unites with bromine to form a mixture of two dibromides. One of these, a liquid, is the 1,2-dibromide, $CH_2BrCHBrCH{=}CH_2$, its structure being proved by ozonization. The other is a solid compound, m. p. 53–54°, proved by Thiele to possess the 1,4-structure, $CH_2BrCH{=}CHCH_2Br$. Farmer further showed that when either the 1,2- or 1,4-dibromide is heated for a few minutes at 100°, the product is a mixture in which the two isomerides appear to be in equilibrium, the equilibrium mixture consisting of 20% of the 1,2- to 80% of the 1,4-isomer. At room temperature the change is very slow. The equilibrium depended in a large measure on the solvent used. Previous to the publication of Farmer's work one of us (M) had determined the same equilibrium between the two dibromide isomers of butadiene and found the equilibrium mixture of the pure compounds to consist of 18% of the 1,2-dibromide to 82% of the 1,4-isomer.

The addition of hydrogen bromide to butadiene was studied by Ipatiew,[10] who obtained an unsaturated bromide, C_4H_7Br, but he was not able to determine its structure.

Lebedev[11] studied the catalytic reduction of butadiene and found that both double bonds are attacked but not at the same rate.

Diels and Alder[12] have found that butadiene will add maleic anhydride, and similar compounds containing the group $C{=}C{-}C{=}O$, in the 1,4-position. The exact mechanism of this reaction is not yet fully understood.

These are the only investigations of the addition reactions of butadiene which have been reported in the literature. As a continuation of our studies on the addition reactions of conjugated systems we have investigated the chlorination of butadiene.

On chlorinating butadiene in carbon disulfide, ligroin or chloroform solution, a mixture of two dichlorides and two tetrachlorides was obtained. The pure dichlorides are colorless oils and distil, under 40 mm. pressure, at 45–45.5° and at 75–76°, respectively. One of the tetrachlorides is an oil, b. p. 110–111° under 40 mm. pressure, while the second tetrachloride, which distilled at 130–134° under 40 mm. pressure, crystallized to a solid, m. p. 72°, which is the same melting point recorded by Henninger[13] for the

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[7] Griner, *Compt. rend.*, 116, 723 (1893); 117, 553 (1893).

[8] Thiele, Ann., 308, 333 (1899).

[9] Farmer, Lawrence and Thorpe, J. *Chem. Soc.*, 729 (1928).

[10] Ipatiew, J. *prakt. Chem.*, [2] 67, 420 (1903).

[11] Lebedev, *J. Chem. Soc.*, 2190 (1928).

[12] Diels and Alder, Ann., 460, 98 (1928).

[13] Henninger, Ann. *chim.*, [6] 7, 229 *(1886).*

tetrachlorobutane he obtained on treating erythritol with phosphorus pentachloride.

The structures of the two dichlorides were proved by oxidation. Three dichlorides are theoretically possible, one 1,2-addition compound and two 1,4-addition compounds, the cis and trans isomers. On ozonizing the lower-boiling dichloride it was possible to isolate α,β-dichloropropionic aldehyde. This proves that the lower-boiling dichloride has the structure $CH_2ClCHClCH{=}CH_2$, and was formed by the 1,2-addition of chlorine to butadiene. The 1,2-structure of the dichloride was further confirmed by oxidizing it with potassium permanganate in dilute alcoholic solution. α,β-Dichloropropionic acid was isolated from the reaction product.

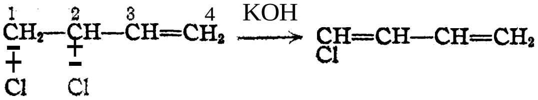
On oxidizing the higher-boiling dichloride with ozone or potassium permanganate in dilute alcoholic solution, it was possible to isolate in each case chloro-acetic acid. This proves that the higher-boiling dichloride has the 1,4-structure, $CH_2ClCH{=}CHCH_2Cl$.

When the lower-boiling dichloride is further chlorinated to the tetrachloride, the liquid tetrachloride is formed to the exclusion of the solid isomer. On the other hand, the higher-boiling dichloride absorbs a molecule of chlorine to give a preponderance of the solid tetrachloride with some of the liquid isomer.

Samples of the two dichlorides and of the two tetrachlorides were reduced with powdered zinc in alcohol. In each case butadiene was formed; this was identified as the tetrabromide, m. p. 114°.

It was possible to control the chlorination of butadiene so that the dichlorides were formed almost exclusively. The detailed procedure will be found in the Experimental Part. From the results of a large number of such chlorinations it appeared that about twice as much of the 1,2-dichloride was formed as of the 1,4-dichloride.

If either of the dichlorides, the 1,2- or 1,4-isomer, is heated to about 90° with twice its weight of dry powdered potassium hydroxide, a vigorous reaction occurs, and a lower-boiling dichloride distils over. After several fractionations a colorless liquid was obtained, b. p. 85° under ordinary pressure, which proved to be monochlorobutadiene, $CHCl{=}CHCH{=}CH_2$. It polymerized on standing to a dark resinous mass. Since the 1,2-dichloride gives the same monochloride as does the 1,4-dichloride, we must conclude that the chlorine atom on carbon atom 2 must be relatively electronegative with respect to the chlorine atom on carbon atom 1, and therefore the terminal carbon atom, 1, must be electronegative relative to carbon atom 2.



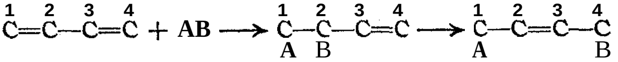
$$\underset{\underset{Cl}{\mp}}{\overset{1}{CH_2}}-\underset{\underset{Cl}{\pm}}{\overset{2}{CH}}-\overset{3}{CH}=\overset{4}{CH_2}\xrightarrow{KOH}\underset{Cl}{CH}=CH-CH=CH_2$$

Since many of the more recent interpretations of the addition reactions of conjugated systems are based on the assumption that the formation of 1,4 addition compounds is not due to a direct addition in the 1,4-position but rather to a rearrangement from the 1,2- or 3,4-compound, it was of considerable importance to determine whether the 1,2-dichloride was spontaneously converted into the 1,4-dichloride. In the first part of this paper reference was made to the fact that the 1,2- and 1,4-dibromides of butadiene were actually in equilibrium with each other, the change of one isomer to the other occurring slowly at room temperature but very rapidly at 100°. The change of the dichlorides into each other, if it occurred, could be followed readily by means of their refractive indices: the refractive index of the 1,2-dichloride is 1.4550 at 30.5°, and of the 1,4-dichloride, 1.4745 at 30.5°.

There was no change in the refractive indices of either of the dichlorides even after they were heated to 90° in a sealed tube for four hours, and we must therefore conclude that even under these conditions the dichlorides are stable and do not rearrange into one another.

In attempting to explain addition reactions to conjugated systems in which 1,2- 1,4- and 3,4-addition takes place, some chemists have suggested an extension of Thiele's theory from the point of view of electronic theories of polarization. According to this theory a conjugated system may polarize in two ways, $\overset{+}{C}—\overset{-}{C}—C—C$ and $\overset{+}{C}—C—C—C$, leading to reaction at adjacent (1,2 or 3,4) or terminal (1,4) carbon atoms of the chain. This theory is little more than a translation of Thiele's partial valencies into more modern terminology.

Gillet[14] has applied the principles of α,γ-rearrangements to conjugated systems and has suggested that the formation of 1,4-addition compounds is preceded by the formation of 1,2-addition compounds, as follows



$$\overset{1}{C}=\overset{2}{C}—\overset{3}{C}=\overset{4}{C} + AB \longrightarrow \underset{A}{\overset{1}{C}}—\underset{B}{\overset{2}{C}}—\overset{3}{C}=\overset{4}{C} \longrightarrow \underset{A}{\overset{1}{C}}—\overset{2}{C}=\overset{3}{C}—\underset{B}{\overset{4}{C}}$$

That this theory is not applicable to all 1,4-addition reactions of conjugated systems has been clearly shown above in the chlorination of butadiene, since the formation of 1,4-butadiene dichloride certainly could not have resulted from the rearrangement of the 1,2-isomer.

Prevost,[15] as a result of his work on conjugated systems, has included both of these possibilities in his interpretation of the addition reactions of conjugated systems, and his views are therefore open to the same criticism.

Farmer,[16] who has made an extended investigation of the addition reactions of conjugated systems, suggests the following mechanism for the bromination of butadiene

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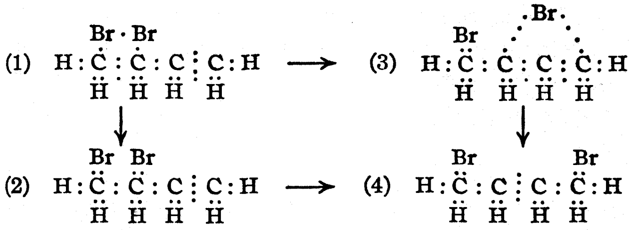
[14] Gillet, *Bull. soc. chim. Belg.*, *31*, 366 (1922).

[15] Prevost, Ann. chim., [10] 10, 113 (1928).

[16] Farmer, *J. Chem. Soc*, 729 (1928).



in which he assumes that the first step in the reaction is the molecular addition of bromine to one of the double bonds in butadiene with the formation of the intermediate compound (1). "This has only transient existence, and breaking of the single linkage between the bromine atoms allows activity in two ways: (a) taking the course normal in the bromination of ethylenes, yielding (2), (b) bringing into action the tautomeric capacity of the propene system and passing through (3) to (4)."

Ingold[17] has classified the addenda in conjugated systems "into three categories'according to whether (Case I) both parts are stable as anions (e. g., Br_2), (Case II) one part is stable as an anion and the other as a kation (e. g., HBr, HCN), or (Case III) both parts are stable as kations (e. g., H_2)." In discussing Case I he states that in the addition of halogens to a conjugated system in a non-ionizing medium, the *initial* product formed could only be a 1,2-addition compound; the formation of any 1,4-compound would, therefore, result from the rearrangement of the 1,2-compound.

In our studies on the chlorination of butadiene, the chlorination was carried out in non-ionizing solvents (carbon disulfide, chloroform and ligroin) and in each case considerable 1,4-dichloride was formed. Since we have shown that the two dichlorides do not rearrange into one another, it is clear that the interpretation advanced by Ingold cannot explain the formation of 1,4-butadiene dichloride in a non-ionizing solvent.

One of the principal objects in this investigation of the addition reactions of conjugated systems has been to show that these addition reactions could be interpreted without recourse to any special hypothesis of conjugation. Conjugated systems differ from non-conjugated systems only in so far as the former may exhibit α,γ-rearrangements, while the latter cannot exhibit this phenomenon.

It has been quite definitely established that the addition of both components of the addendum to an ethylenic double bond does not occur simultaneously. It is more likely, as has been suggested by Stieglitz,[18] that the essential feature is the attraction of the positive substituting group to the negative carbon valencies irrespective of complete saturation. Confirmatory evidence for this hypothesis has been brought by Terry and Eichel-

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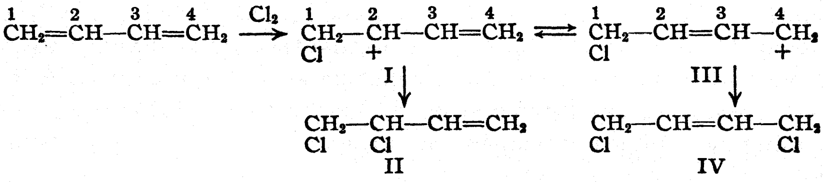
[17] Ingold, *J. Chem. Soc.*, 910 (1928); 2022 (1929).

[18] Stieglitz, THIS JOURNAL. 44, 1304 (1922).

berger[19] and by Francis,[20] who have shown that in the addition of halogens to unsaturated compounds the halogen molecule initially supplies only one halogen atom, the positively charged halogen atom, to the unsaturated substance.

Applying these same principles to the chlorination of butadiene we would have as the first step of the reaction the addition of the positive chlorine atom to the terminal carbon atom (see equation on page 4046 to give I).



$$\overset{1}{CH_2}{=}\overset{2}{CH}{-}\overset{3}{CH}{=}\overset{4}{CH_2} \xrightarrow{Cl_2} \underset{Cl}{\overset{1}{CH_2}}{-}\underset{+}{\overset{2}{CH}}{-}\overset{3}{CH}{=}\overset{4}{CH_2} \rightleftharpoons \underset{Cl}{\overset{1}{CH_2}}{-}\overset{2}{CH}{=}\overset{3}{CH}{-}\underset{+}{\overset{4}{CH_2}}$$

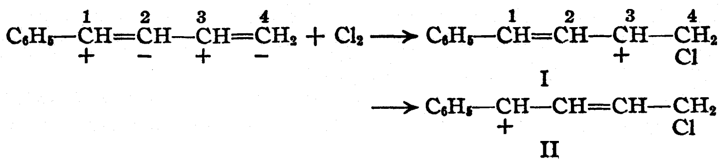
$$\text{I} \downarrow \qquad \text{III} \downarrow$$

$$\underset{Cl}{CH_2}{-}\underset{Cl}{CH}{-}CH{=}CH_2 \;(\text{II}) \qquad \underset{Cl}{CH_2}{-}CH{=}CH{-}\underset{Cl}{CH_2} \;(\text{IV})$$

In the second phase of this reaction the negative chlorine atom either may satisfy the positive charge on carbon atom 2 to give II, 1,2-butadiene dichloride, in a manner normal to ordinary ethylenic compounds; or this intermediate I may undergo a typical α,γ-rearrangement to III, and the negative chlorine atom would now add to the 4 carbon atom to give IV, 1,4-butadiene dichloride.

The formation of either the 1,2- or 1,4-isomer would then depend on the equilibrium of the two intermediates, I and III. This equilibrium would in turn depend on the effect of the group CH_2Cl, in this case, and upon the experimental environment, such as solvent, etc., in promoting or hindering this α,γ-rearrangement. Ingold and his students have, for some years, studied very extensively the effect of various groups in causing such rearrangements to take place, and they have found that the groups CH_2Cl– and CH_2Br– favor such rearrangements. This theory would suggest that ionization should occur preliminary to an α,γ-rearrangement. This would explain why the 1,2- and 1,4-dibromides rearrange into each other while the corresponding dichlorides do not, since it is well known that the C–Br bond is much easier to break than the C–Cl bond.

The chlorination of phenylbutadiene could be formulated as follows, employing the electronic formula for phenylbutadiene developed by Muskat and Becker[1]



$$C_6H_5{-}\underset{+}{\overset{1}{CH}}{=}\underset{-}{\overset{2}{CH}}{-}\underset{+}{\overset{3}{CH}}{=}\underset{-}{\overset{4}{CH_2}} + Cl_2 \longrightarrow C_6H_5{-}\overset{1}{CH}{=}\overset{2}{CH}{-}\underset{+}{\overset{3}{CH}}{-}\underset{Cl}{\overset{4}{CH_2}} \;(\text{I})$$

$$\longrightarrow C_6H_5{-}\underset{+}{CH}{-}CH{=}CH{-}\underset{Cl}{CH_2} \;(\text{II})$$

We would not expect to find addition taking place, in the first phase, to the 2 carbon atom, since it is well known that phenyl groups attached to a

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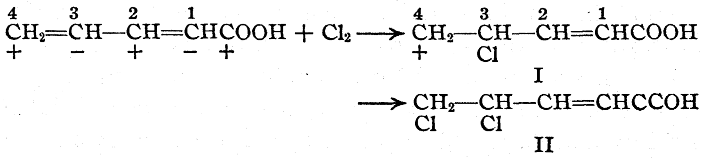
[19] Terry and Eichelberger, THIS JOURNAL, 47, 1067 (1925).

[20] Francis, *ibid.*, 47, 2344 (1925).

double bond hinder addition to that double bond. Now, however, the effect of the phenyl group in retarding such a rearrangement I ⟶ II is far greater than the effect of the CH_2Cl group in promoting this rearrangement, and, consequently, we should expect chlorination to occur mostly in the 3,4-position. This is in agreement with the results of Muskat and Huggins,[1] who found that phenylbutadiene absorbs chlorine in the 3,4-position.

The chlorination of vinylacrylic acid presents a somewhat different condition. Again, employing the electronic formula for vinylacrylic acid developed by Muskat and Becker,[1] we see that the carbon atoms 1 and 3 are the only ones that could react in the first phase with the positive chlorine atom. Since a,@-unsaturatedacids are known to add halogen with considerably more difficultythan do the corresponding @ y- or γ,δ-unsaturated acids



$$\overset{4}{\underset{+}{CH_2}}=\overset{3}{\underset{-}{CH}}-\overset{2}{\underset{+}{CH}}=\overset{1}{\underset{-}{CH}}\underset{+}{COOH}+Cl_2\longrightarrow\underset{\text{I}}{\overset{4}{\underset{+}{CH_2}}-\overset{3}{\underset{Cl}{CH}}-\overset{2}{CH}=\overset{1}{CH}COOH}$$

$$\longrightarrow\underset{\text{II}}{\underset{Cl}{CH_2}-\underset{Cl}{CH}-CH=CHCCOH}$$

we should expect carbon atom 3 to be attacked by chlorine in preference to carbon atom 1. This is borne out by the fact that we were not able to prepare a tetrachloride of vinylacrylic acid from the 3,4-dichloride. The first step of the chlorination of vinylacrylic acid would be represented as above. Now, however, the interme ate I cannot undergo an α,γ-rearrangement and the negative chlorine atom must add to the terminal carbon atom to give a 3,4-dichloride exclusively. This is in perfect agreement with the results of Muskat, Becker and Lowenstein[1] on the chlorination and bromination of vinylacrylic acid in which they obtained only 3,4-addition products.

This same theory would apply equally well to the addition of HX and HOX to conjugatedsystems. An extension of this theory to reduction and oxidation of conjugated systems will be presented in a later paper.

Experimental Part

The Preparation of **Butadiene.**—The preparation of butadiene as finally developed consisted of three major operations: (1) converting butyl alcohol into butyl chloride, (2) chlorinating butyl chloride to dichlorobutane and (3) converting dichlorobutane into butadiene by passing it over heated soda lime.

(1) n-Butyl alcohol was converted into n-butyl chloride according to the method of Norris[6] by heating the alcohol with concentrated hydrochloric acid and anhydrous zinc chloride.

(2) The pure butyl chloride was then chlorinated to the dichloride by allowing the vapors of butyl chloride to react with chlorine gas under the influence of light. Perkin[6] describes an apparatus, which he used for this purpose, but we have remodeled and improved this apparatus so that it gives a much better yield of the chlorinated product and requires very little attention. In Fig. 1 is shown the chlorinating apparatus that was

used. **A** is a three-liter round-bottomed flask which contains two liters of butyl chloride heated on an electric plate. A thermometer B is immersed in the liquid in flask **A;** this gives the distillation temperature of the liquid. As the chlorination proceeds the distillation temperature of the liquid rises, and it is thus possible to follow the extent of the reaction. C is a heat insulated Vigreux column (about 40 cm. long), and D is the reaction tube where the chlorine gas and the vapors of the butyl chloride are mixed. The mixed vapors are carried on up the tube and are exposed to the light coming from a 1000-watt lamp placed at X. Under the influence of the light reaction occurs with the formation of the higher-boiling dichlorobutane. F is a bulb reflux condenser so designed that the openings of the bulbs are large at the bottom, where most of the condensation occurs, and become gradually smaller as they approach the top, where the condensate is slight. This type of condenser is very efficient for any purpose in which a great deal of condensate is formed. The hydrogen chloride vapors pass through the reflux condenser F and are absorbed over water. The butyl chloride in A is heated to boiling; when the butyl chloride vapors have filled tube D, the chlorine is allowed to pass in through **E** and the 1000-watt lamp is turned on. The chlorine is passed in through a flowmeter and a sulfuric acid washbottle at a rate, calculated for standard conditions, of 1120 cc. of chlorine per minute. The course of the reaction is followed by the thermometer B. At the beginning of the chlorination the temperature is 77°, the boiling point of butyl chloride. As the distillation proceeds the distillation temperature of the liquid in A rises. The chlorination is allowed to proceed until the temperature reaches 115°. This requires about six hours. If the temperature is allowed to go much higher than 115° some higher chlorinated products are formed. The time could be reduced even more if the reflux condenser F was made larger than the one we actually used. After the reaction was over the chlorinated mixture was roughly fractionated through a column one meter long filled with glass beads. The results of four such runs are recorded in Table I. In each run 2000 cc. (about 1775 g.) of butyl chloride was used. and the chlorination was continued at a constant rate for about six hours, allowing the distillation temperature to rise to 115".

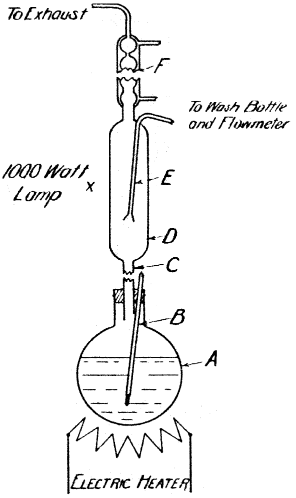


Fig. 1.

TABLE I

CHLORINATION EXPERIMENTS ON BUTYL CHLORIDE

Run no.	1 77–110°, g.	2 110–120°, g.	3 120–130°, g.	4 130–140°, g.	5 140–150°, g.	6 150–165°, g.	Residue, g.
1	242	330	503	546	166	132	100
2	382	300	472	552	191	127	114
3	392	252	418	516	169	138	100
4	292	345	500	540	207	122	107

Fraction 1 (77–110°) contains mostly unreacted butyl chloride and some of the lower dichlorides. Fraction 2 (110–120°) may very likely contain α,α-dichlorobutane, b. p. 114'. Fraction 3 (120–130") contains most of the α,β-dichlorobutane, b. p. 125°. Fraction 4 (130–140°) contains most of the α,γ-dichlorobutane, b. p. 134–137°. Fraction 6 (150–165°) contains most of the α,δ-dichlorobutane, b. p. 161–163°. Fraction 5 (140–150°) is probably a mixture of fractions 4 and 6.

It is interesting to note that in the chlorination of butyl chloride α,γ- and α,β-dichlorobutanes are the main products. There is some α,δ- and probably some α,α-dichlorobutane formed.

(3) The different fractions of dichlorobutane were now distilled over heated soda lime, which removed two moles of hydrogen chloride to give butadiene. The apparatus that was used for this purpose is illustrated in Fig. 2. The dichlorobutane was placed in the separatory funnel A and it was allowed to flow through a tube one meter long (in order to give sufficient pressure to force the vapors through the apparatus) into the round-bottomed flask (500-cc.) B, which was heated on an electric plate. The rate of flow of the dichlorobutane and the temperature of the flask B were so controlled that the process was essentially a flash distillation. The dichlorobutane then passed into the steel tube D, which contained coarse soda lime (about 450 g.). The tube was heated to about 700–730° by means of the electric oven E. At this temperature the soda lime removed two moles of hydrogen chloride from the dichlorobutane to give butadiene.

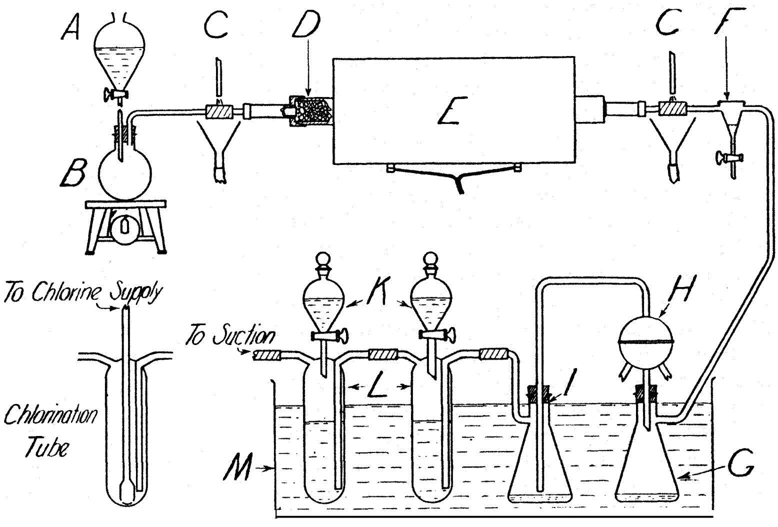


Fig. 2.

The vapors were then passed in succession through the flasks G, ball condenser H and flask I. These flasks were immersed in an ice–salt bath M and served to free the butadiene gas from water, unreacted dichlorobutane and resinous decomposition products. At C water was allowed to run over the rubber connections joining the hot steel tube D to the rest of the apparatus. F is a trap which served to collect a great deal of the water and resinous decomposition products. The butadiene coming from flask I was sufficiently pure to use in our work.

In order to determine which fraction of the dichlorobutane gave the best yield of butadiene, a number of runs were made with each of the fractions of the dichlorides. The butadiene formed was collected as the tetrabromide. For this purpose the butadiene coming from I was passed into the bromination flasks L, which were immersed in the ice–salt bath M. These flasks were about half-filled with chloroform and the bromine was added from the separatory funnels K so that an excess of bromine was always present. Usually the absorption was complete in the first flask but the second flask was used in order to prevent any possible loss of butadiene. In order to overcome the pressure in the system, a slight suction was applied at the end of the second bromination flask. At the completion of the run the brominated mixture was removed from the flasks and warmed under diminished pressure to remove any excess bromine and chloroform. At this stage some solid butadiene tetrabromide would crystallize out of solution. This was removed and the filtrate was subjected to fractional distillation under 50 mm. pressure. From the lower-boiling fractions of the chlorinated butyl chloride considerable dibromobutane distilled over at 75–82° under 50 mm. pressure. This is no doubt due to some unchanged butyl chloride still present in the chlorinated mixture, which is converted into 1-butene by the hot soda lime and which in turn is brominated to 1,2-dibromobutane. After all of the dibromobutane had distilled over, the temperature rose quickly to about 145°, at which temperature the lower-boiling stereoisomeric tetrabromide of butadiene distilled over. The temperature then rose to 175°, at which temperature the pure solid tetrabromide, m. p. 117°, distilled. The fraction from 145–175° consisted of a mixture of the two tetrabromides. From the higher-boiling fractions of the chlorinated butyl chloride the two stereoisomeric tetrabromides alone were obtained. From the combined filtered and distilled butadiene tetrabromides the yield of butadiene was calculated. In Table II are recorded the yields of butadiene obtained from 200 g. of each of the chlorinated fractions. About one hour was required for each run. Two runs were made on each fraction.

TABLE II

PERCENTAGE OF BUTADIENE OBTAINED FROM EACH OF THE CHLORINATED FRACTIONS

	1 75–110° g.	2 110–120°, g.	3 120–130°, g.	4 130–140°, g.	5 140–150°. g.	6 150–165°, g.
Butadiene tetrabromide obtained, g..........	40	118	148	174	139	146
	41	104	144	174	...	157
Yield of butadiene, %..	6.9	18.8	24.8	29.6	23.6	25.6

It is thus seen that the α,γ-dichlorobutane gave the best yield of butadiene, 29.6% of the theoretical.

The Chlorination of Butadiene.—The butadiene coming from I was passed into the chlorination tube shown in the diagram. Usually two such chlorination tubes were used and these were immersed in the ice–salt bath M. The tubes were about half filled with carbon disulfide and a slow stream of chlorine gas was passed in. At the completion of the run (about one hour for 200 g. of dichlorobutane) the chlorinated mixture was removed and freed from carbon disulfide by means of suction. The residual oil was subjected to fractional distillation. After several redistillations four fractions were collected under 40 mm. pressure: (a) 45–45.5°, (b) 75–76°, (c) 110–111°, (d) 130–134°. Each fraction was analyzed for chlorine; the first two fractions proved to be dichloro addition compounds of butadiene, while the last two fractions proved to be tetrachloro addition compounds of butadiene.

It was possible to control the chlorination of butadiene so that the dichlorides were formed almost exclusively. This was accomplished by allowing the butadiene to pass into the chlorination tubes at a more rapid rate than the chlorine. This was usually accompanied by a loss of some of the butadiene. If the chlorine was allowed to pass in at a fairly rapid rate, or if the reaction was allowed to warm up, the tetrachlorides of butadiene were formed exclusively. In one experiment the pure butadiene was chlorinated directly, without any solvent, at about –75° and the same products were formed.

1,2-Dichlorobutadiene.—The lower-boiling dichloride is a colorless oil. It distils at 45–45.5° under 40 mm. pressure and at 115° under atmospheric pressure, without decomposition. Its refractive index was determined with an Abbé refractometer; at 30.5° its refractive index is 1.4550.

Anal. Calcd. for $C_4H_6Cl_2$: Cl, 56.75. Found: Cl, 56.73, 56.80.

The structure of the lower-boiling dichloride (a) was determined by ozonization. Considerable difficulty was experienced in isolating the oxidized fragments. Its identification was finally effected by ozonizing the pure dichloride, without any solvent, and keeping the temperature of the oxidation reaction at about 0°. After the ozonization was complete, water was added to the viscous ozonide, and it was warmed on the water-bath to decompose it. The aldehydes were taken up in ether and washed several times with dilute alkali to remove any acids. If the ozonization was not allowed to continue too long, only negligible quantities of acids were formed. The ethereal solution was dried over sodium sulfate, the ether removed by suction, and the residual oil was distilled under diminished pressure. Most of it distilled over at 73° under 50 mm. pressure, the boiling point of α,β-dichloropropionic aldehyde. This was further identified by treating with sodium acetate according to the method of Piloty and Stock,[21] which converted the dichloride into a-chloro-acrolein. This distilled over at 40° under 30 mm. pressure, the recorded boiling point of a-chloro-acrolein. The water solution remaining from the ethereal extract gave the usual color tests for formaldehyde. This proved that the lower-boiling dichloride (a) has the 1,2-structure, $CH_2ClCHClCH{=}CH_2$.

This structure was further confirmed by oxidizing the lower dichloride with potassium permanganate in dilute alcoholic solution. An acidic oil was obtained which crystallized on standing to a solid melting at 50°, the recorded melting point of α,β-dichloropropionic acid.

1,4-Dichlorobutadiene.—The higher-boiling dichloride (b), when first distilled, is a yellow oil with a pungent odor, but after several distillations it is obtained as a colorless oil with a very faint odor. It distils at 75–76° under 40 mm. pressure and at about 145° under atmospheric pressure without decomposition. Its refractive index was determined with an Abbé refractometer; its refractive index is 1.4745 at 30.5°.

Anal. Calcd. for $C_4H_6Cl_2$: Cl, 56.75. Found: Cl, 56.84, 56.97.

The structure of the higher-boiling dichloride (b) was determined in a manner entirely analogous to the method used for the lower-boiling dichloride. However, in this case, no difficulty was encountered in working up the products of oxidation. A number of oxidation experiments were carried out both with ozone and potassium permanganate and in every case a good yield of chloro-acetic acid was isolated. This was identified by its melting point, 62°, and the melting point of a mixture with a sample of known origin. This proves that the higher-boiling dichloride has the 1,4-structure, $CH_2Cl-CH{=}CHCH_2Cl$.

Tetrachlorobutanes.—Fractions (c) and (d) are the two stereoisomeric tetrachlorobutanes. Fraction (c) is a colorless oil with a faint odor. It distils at 110–111° under 40 mm. pressure.

Anal. Calcd. for $C_4H_6Cl_4$: Cl, 72.41. Found: Cl, 72.49, 72.57.

Fraction (d) crystallized to a solid which melted at 72°.

Anal. Calcd. for $C_4H_6Cl_4$: Cl, 72.41. Found: Cl, 72.64. 72.55.

Reduction of the Di- and Tetrachlorides of Butadiene.—Samples of each of the dichlorides and of the tetrachlorides were reduced with powdered zinc and alcohol according to the method of Thiele.[8] In each case butadiene was formed, which was identified as the tetrabromide, m. p. 114°. This proves that these chlorides are true addition products of butadiene.

1-Chlorobutadiene.—If either of the dichlorides, the 1,2- or 1,4-isomer, is heated to about 90° with twice its weight of powdered potassium hydroxide, a vigorous reaction occurs, and a lower-boiling chloride is formed and distils over through a condenser which is attached to the reaction flask. After several fractionations a colorless liquid is ob-

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[21] Piloty and Stock, Ber., 31, 1385 (1898).

tained which boils at 85° under atmospheric pressure. It polymerized on standing to a dark resinous mass. It was analyzed for chlorine and proved to be the monochloride, $CHCl{=}CHCH{=}CH_2$.

Anal. Calcd. for C_4H_5Cl: Cl, 40.07. Found: Cl, 39.99, 40.08.

Attempted Rearrangements of the Two Dichlorides.—Samples of each of the dichlorides, the 1,2- and 1,4-isomers, were allowed to stand for several weeks at room temperature (about 25–30°) but no change in their refractive indices occurred. They were then redistilled several times at atmospheric pressure, and their refractive indices were again measured, but no change could be detected. Finally, samples of each were sealed in bomb tubes and heated for four hours at 90°. There was no change in the index of refraction of either of the two dichlorides and we must therefore conclude that even at 90° and under pressure the dichlorides are stable and do not rearrange into one another.

Summary

1. An improved method for the preparation of butadiene starting from *n*-butyl alcohol is given, including a detailed description of the apparatus used.

2. On chlorinating butadiene a mixture of two dichlorides and two tetrachlorides is obtained. The structures of the two dichlorides were proved by oxidation experiments: the lower-boiling dichloride, b. p. 45–45.5' under 40 mm. pressure, is a 1,2-dichloride—$CH_2ClCHClCH{=}CH_2$; the higher-boiling dichloride, b. p. 75–7G°, is a 1,4-dichloride—$CHClCH{=}CHCH_2Cl$. The two stereoisomeric tetrachlorides distilled at 110–111° and 130–134°, respectively. The latter crystallized to a solid, m. p. 72°.

3. It was definitely established that the two dichlorides did not rearrange into each other even at 90° and under pressure.

4. On heating either of the dichlorides with solid potassium hydroxide a monochloride, b. p. 85° under atmospheric pressure, is formed. Its structure is $CHCl{=}CHCH{=}CH_2$.

5. A theory to interpret the addition reactions of conjugated systems without recourse to any special hypothesis of conjugation is presented.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO ALKYL TIN COMPOUNDS. IV. PROPERTIES OF THE COMPLEX HYDROXY BROMIDE, $[(CH_3)_3SnOH]_2 \cdot (CH_3)_3SnBr$

BY CHARLES A. KRAUS AND RALPH H. BULLARD

RECEIVED JULY 9, 1930 PUBLISHED OCTOBER 6, 1930

As mentioned in a preceding article of this series, Kraus and Harada[1] have prepared compounds of the type $[(CH_3)_3SnOH]_2 \cdot (CH_3)_3SnX$ where X is a halogen. These compounds are readily obtained in the form of well-defined crystals and preliminary investigation indicated that they have measurable stability in solution. It appeared of interest to study these compounds in order to gain some knowledge as to the nature of the complex formed. Dissolved in alcohol or acetone, the compounds conduct the electric current with considerable facility much better than corresponding solutions of trimethyl tin halide or trimethyl tin hydroxide. This indicates that a complex cation of some kind is formed which is moderately electropositive. On treating the compound with silver hydroxide in aqueous solution, an hydroxy derivative of the complex cation was obtained which has approximately the same strength as trimethyl tin hydroxide. However, as indicated by conductance measurements, this complex hydroxide, which is isomeric with trimethyl tin hydroxide, gradually breaks down to form the latter compound.

While the precise nature of the complex cation has not, as yet, been determined, it seems fairly clear that it contains three trimethyl tin groups along with two hydroxy groups. The nature of the linkage is uncertain. That trimethyl tin hydroxide is involved, perhaps after the manner of an oxonium compound, seems fairly certain. This is further borne out by the fact that trimethyl tin hydroxide reacts with methyl iodide to yield a compound whose ionization is considerably higher than that of either of its constituents.

Preparation and Properties of $[(CH_3)_3SnOH]_2 \cdot (CH_3)_3SnBr$.—The compound may be prepared by a variety of methods. According to Callis[2] it is formed by the action of oxygen on trimethyl tin iodide in the sunlight. As will be shown below, it may also be formed by the oxidation of trimethyl tin in the presence of trimethyl tin bromide and water in benzene solution. It is most conveniently prepared by adding two equivalents of trimethyl tin hydroxide to one of the corresponding bromide (or another halide) in various solvents. We have found chloroform the most convenient solvent for this purpose.

One mole of trimethyl tin bromide is treated with two moles of trimethyl tin hydroxide in chloroform at room temperatures. Reaction takes place immediately with

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[1] Kraus and Harada, THIS JOURNAL, 47,2416 (1925).

[2] Callis, Dissertation, Clark University, 1922.

the formation of a supersaturated solution of the compound, which crystallizes out slowly on standing, large, well-formed crystals being produced. On vigorously shaking the solution, the greater proportion of the compound is immediately precipitated in the form of fine crystals, while the remainder of the material crystallizes out as the chloroform evaporates. The crystals so prepared are quite pure and melt sharply at 116° with slow decomposition. They appear to be identical with the compound prepared by Kraus and Harada.[1] Crystals of the compound, prepared and purified by various methods, were analyzed for bromine and tin. The results of the analyses were the same for the various preparations.

Anal. Subs., 0.4503, 0.5277, 0.4819: AgBr, 0.1398, 0.1641, 0.1496. Calcd. for $[(CH_3)_3SnOH]_2(CH_3)SnBr$: Br, 13.17. Found: Br, 13.21, 13.23, 13.21; mean, 13.22. Subs., 0.4229, 0.4120, 0.5124: SnO_2, 0.3159, 0.3076, 0.3736. Calcd.: Sn, 58.83. Found. Sn, 58.84, 58.81, 58.97; mean 58.87.

The results of the analyses indicate that the composition of the compound corresponds to the formula $[(CH_3)_3SnOH]_2\cdot(CH_3)_3SnBr$.

The formula of the compound may be written $[(CH_3)_3Sn]_3OBr\cdot H_2O$. This would correspond to an oxonium type of compound containing one molecule of water. The attempt was made to prepare an anhydrous compound corresponding to this formula For this purpose, equivalent amounts of trimethyl tin and trimethyl tin bromide were dissolved in dry benzene under an atmosphere of oxygen. A control experiment was carried out in which moist benzene was employed as solvent. The apparatus was attached to a manometer so that the rate of absorption of oxygen could be measured. Absorption of oxygen took place in both experiments, the rate in moist benzene being about twice that in the dry solvent. In the dry benzene, a white amorphous powder was precipitated, which appeared to be trimethyl tin oxide. In moist benzene, crystals were formed which closely resembled the dihydroxy bromide.[3] Unfortunately, this sample was lost and an analysis of the crystals could not be made. The experiments indicate, however, that, while the dihydroxy bromide is formed in the presence of moisture, it is not formed in the dry solvent.

Some Reactions of $[(CH_3)_3SnOH]_2\cdot(CH_3)_3SnBr$

Reduction with Metallic Sodium in Liquid Ammonia.—If the dihydroxy bromide contains one molecule of water as such, we should expect that, on reduction with metallic sodium in liquid ammonia, hydrogen would be evolved and sodium hydroxide precipitated. On the other hand, if hydroxyl groups are present in combination with tin, sodium hydroxide should be formed without evolution of hydrogen, while the trimethyl tin group should be reduced to the corresponding stannide, $NaSn(CH_3)_3$.

A quantity of the dihydroxy bromide (1.526 g.) was dissolved in liquid ammonia, a clear colorless solution being formed. On adding sodium, reaction took place immediately with the precipitation of a white solid which was doubtless trimethyl tin. On further addition of sodium, this solid dissolved, yielding a solution having a faint yellow color. This color is characteristic of sodium trimethyl stannide,[4] which is formed by the action of sodium on trimethyl tin, As the reaction proceeded, a gelatinous precipitate was formed which was doubtless sodium hydroxide. Sufficient sodium was added to impart a permanent blue color to the solution.

In the course of the reaction a small quantity of gas was evolved which was collected

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[3] Since accepted rules for the nomenclature of compounds of this type have not been elaborated, the complex compounds of the type $[(CH_3)_3SnOH]_2\cdot(CH_3)_3SnX$ will for convenience be termed "dihydroxy halides."

[4] Kraus and Sessions, THIS JOURNAL, 47, 2361 (1925).

over water. Assuming the compound to contain one molecule of water, 28 cc. of hydrogen should have been produced. In the experiment 9 cc. of hydrogen was collected This was given off slowly throughout the course of the reaction. Since the volume of hydrogen found was much below that required for one molecule of water per mole of compound, we must conclude that hydroxyl groups are present in the compound, which, for the most part, are split off on addition of sodium with the formation of sodium hydroxide.

Reaction with Ammonia.—It was suspected that, in a solution of the dihydroxy bromide, there exists an equilibrium between free trimethyl tin hydroxide and trimethyl tin bromide. If such is the case, then on treating the compound with ammonia in a suitable solvent, ammino trimethyl tin bromide, $(CH_3)_3SnBr\cdot NH_3$, should be formed and, if insoluble, precipitated.[6]

A quantity of the dihydroxy bromide was dissolved in chloroform and ammonia gas was passed through the solution. A precipitate was immediately formed. This was thrown on a filter and the excess chloroform evaporated. The resulting solid sublimed on heating and answered to tests for ammino trimethyl tin bromide.

Although ammino trimethyl tin bromide is precipitated under the conditions of the experiment just described, when the dihydroxy bromide is dissolved in liquid ammonia, little change occurs. A quantity of the compound was dissolved in liquid ammonia, the solvent was allowed to evaporate and the melting point of the residue determined. The substance melted at 107°, while the original pure dihydroxy bromide melted at 115°. Apparently, on solution in liquid ammonia, only an inconsiderable amount of the material was transformed. Other properties of the residue, such as the products of thermal decomposition, remained unchanged on treating with liquid ammonia. It seems that in liquid ammonia solution the compound is not extensively dissociated into its constituents.

Thermal Decomposition.—When the compound is heated under atmospheric pressure, it melts at 115° to form a clear liquid which boils slowly, giving a distillate containing trimethyl tin bromide. This was shown by collecting the distillate, dissolving it in ether, and precipitating the bromide as ammino trimethyl tin bromide by means of ammonia.

A weighed quantity of the compound was introduced into one leg of an inverted U-tube, which was then evacuated. The limb containing the compound was heated, while the other limb was cooled in liquid ammonia. In this experiment. 3.226 g. of compound was subjected to sublimation. Most of the material sublimed to the cooler parts of the tube above the oil-bath. A small quantity of solid residue was left behind, while some liquid was collected in the second limb of the U-tube. Of the total material, 3.0731 g. was found in the sublimate and 0.0428 g. in the residue. By difference, the weight of the distillate was 0.110 g.

The solid residue was analyzed for tin by the modified Krause method.'

Using 23.3 mg. of the residue, 29.9 mg. of SnO_2 was obtained, corresponding to 70.68% of tin, as compared with 72.04% required for dimethyl tin oxide. The sublimate for the most part melted at 115°, the same temperature as the original compound. In the distillate, the presence of both water and tetramethyl tin was established.

It is evident that, on heating the original compound, dissociation takes place according to the equation

$$[(CH_3)_3SnOH]_2\cdot(CH_3)_3SnBr = 2(CH_3)_3SnOH + (CH_3)_3SnBr \qquad (I)$$

When the vapors reach the colder portions of the tube, condensation occurs and the reaction is reversed.

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[5] Kraus and Greer, THIS JOURNAL, 45, 3078 (1923).

[6] Kraus and Bullard, *ibid.*, 51, 3606 (1929).

As was shown in a preceding article: when trimethyl tin hydroxide is heated to a temperature from 80 to 100°, it breaks down according to the equation

$$2(CH_3)_3SnOH = (CH_3)_2SnO + (CH_3)_4Sn + H_2O \qquad (II)$$

In the above experiment, during the process of sublimation, some of the hydroxide decomposed according to this reaction equation, which accounts for the residue of dimethyl tin oxide The dimethyl tin oxide left behind, weighing 0.0428 g., corresponds to 0.108 g. combined weight of tetramethyl tin and water, according to Equation II. The weight of distillate, as determined by difference, was found to be 0.110 g. The water formed on sublimation of the original compound, therefore, resulted from the decomposition of the trimethyl tin hydroxide and not from the loss of water of hydration.

Molecular Weight.—The preceding experiments indicate that the hydroxyl group retains its linkage to tin in the compounds formed between trimethyl tin hydroxide and the trimethyl tin halides. It was surmised that in solution an equilibrium exists between the compound and its constituents. A determination of the molecular weight of the compound in solution should give clear evidence of dissociation, if such exists.

The compound is not sufficiently soluble in benzene to permit of molecular weight determination in that solvent. Accordingly, its molecular weight was determined in naphthalene by the cryoscopic method. The results are given in Table I.

TABLE I

MOLECULAR WEIGHT OF $[(CH_3)_3SnOH]_2\cdot(CH_3)_3SnBr$ IN NAPHTHALENE

Naphthalene, g.	Compd., g.	At	Mol. wt.
23.38	0.3515	0.408	262
26.16	.2358	.254	252

The formula weight of the dihydroxy bromide is 605.3, while that of the corresponding mixture of trimethyl tin hydroxide and trimethyl tin bromide is 201.6. The value obtained for the mean molecular weight in naphthalene shows that the compound is largely dissociated into its constituents in that solvent.

Conductance of Mixtures of $(CH_3)_3SnBr$ and $(CH_3)_3SnOH$ in Solution.—It was thought that a study of the conductance of the dihydroxy bromide and of various mixtures with trimethyl tin bromide in non-aqueous solvents might yield some information as to the existence of a complex compound and its properties. Accordingly, the conductance of such mixtures was studied in absolute alcohol and in acetone. The conductance was measured in suitable cells by the usual Kohlrausch method and with the usual precautions. No claims are made for exceptional precision, since the object of these experiments was to get the general order of magnitude and the course of the conductance curve as a function of the composition of the solution.

Absolute Alcohol.—The conductance of a solution of the dihydroxy bromide was compared with that of an equivalent mixture of its constituents in absolute alcohol. The specific conductance of the alcohol was 0.5 × 10^{-6}. All measurements were carried out at 25°. The results are given in Table II, concentrations being expressed in moles per liter and the specific conductance L in reciprocal ohms.

TABLE II

CONDUCTANCE OF $[(CH_3)_3SnOH]_2 \cdot (CH_3)_3SnBr$ AND OF MIXTURES OF $(CH_3)_3SnOH$ AND $(CH_3)_3SnBr$ IN ABSOLUTE ALCOHOL AT 25°

$(CH_3)_3SnOH$	$(CH_3)_3SnBr$	$[(CH_3)_3SnOH]_2$ $(CH_3)_3SnBr$	L × 10^4
0.03314	0.0	0.0	0.03
.02601	.01657	.0	.87
.03314	.01657	.0	.96
.0	.01657	.0	.54
.0	.0	.01657	.95

As may be seen from the table, a solution of the compound at a concentration of 0.0166 mole per liter has a specific conductance of 0.95 × 10^{-4}, which is substantially identical with that of an equivalent mixture of its constituents. It follows that, when solutions of trimethyl tin hydroxide and bromide are mixed, reaction takes place immediately with the formation of a complex compound. It will be noted that the conductance of the pure hydroxide, at a concentration equivalent to that of hydroxide in a solution of the compound, was only 0.03 × 10^{-4}, while that of a corresponding solution of trimethyl tin bromide was 0.54 × 10^{-4}. In other words, in ethyl alcohol solution, the conductance of the compound is nearly twice as great as the sum of that of its constituents taken separately in the same solvent. The molecular conductance of the compound at a concentration of 0.0166 molar is approximately 5.8.

Acetone.—As Kraus and Callis[7] have shown, the alcohols, or other hydroxy compounds, react with trimethyl tin bromide to form a complex cation which is fairly electropositive and the solutions of which are therefore markedly ionized. It was to be expected, therefore, that, in other types of solvents, the relative conductance of the dihydroxy bromide and of trimethyl tin bromide would differ greatly from that found in alcohol.

The conductance of the dihydroxy bromide was compared with that of various mixtures of the hydroxide and the bromide in acetone at 25°. The specific conductance of the acetone used was 1.2 × 10^{-6}. A solution containing 0.01657 mole of dihydroxy bromide per liter had a specific conductance of 101 × 10^{-6}, while a solution of trimethyl tin bromide at the same concentration had a conductance of only 2.06 × 10^{-6}. The conductance of a solution of the hydroxide of equivalent concentration (0.033 N) was not determined but a 0.1 N solution of the hydroxide was found to have a specific conductance of 5.02 × 10^{-6}. It is evident that

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[7] Kraus and Callis, THIS JOURNAL, 45, 2624 (1923).

the dihydroxy bromide is a much better conductor than either of the constituents at corresponding concentrations. It is noteworthy that, in acetone, trimethyl tin hydroxide is a slightly better conductor than is the corresponding bromide.

A 0.1 *N* solution of trimethyl tin bromide in acetone was made up and varying amounts of hydroxide were added. The specific conductance of these solutions was measured in the usual way. The values are tabulated below.

TABLE III

CONDUCTANCE OF 0.1 *N* $(CH_3)_3SnBr$ IN ACETONE IN THE PRESENCE OF $(CH_3)_3SnOH$

Concn. $(CH_3)_3SnOH$	0.00	0.01	0.02	0.03	0.04	0.05	0.06
Ratio of hydroxide to bromide	0.0	0.1	0.2	0.3	0.4	0.5	0.6
Sp. cond. $\times 10^4$	0.0345	1.13	2.06	2.93	3.73	4.45	5.19
Concn. $(CH_3)_3SnOH$	0.07	0.08	0.09	0.10	0.15	0.20	
Ratio of hydroxide to bromide	0.7	0.8	0.9	1.0	1.5	2.0	
Sp. cond. $\times 10^4$	5.85	6.37	6.88	7.37	9.36	10.73	

As may be seen from the table, on adding trimethyl tin hydroxide to a solution of trimethyl tin bromide in acetone, the conductance is greatly increased. For an addition of one-tenth mole of the hydroxide per mole of bromide, the conductance is increased approximately 30 times, while for an addition of 2 moles it is increased 300 times. It may be pointed out that the final solution, containing 2 moles of hydroxide per mole of bromide, had a molecular conductance of 10.7. This value approaches that of some salts.

A second series of measurements was carried out with solutions containing 0.0166 mole of trimethyl tin bromide and varying amounts of trimethyl tin hydroxide from 0.0 to 0.0833 N. In other words, the ratio of hydroxide to bromide varied from 0.0 to 5.0. The specific conductance of the solutions was corrected for the conductance of the solvent and was approximately corrected for the conductance of excess trimethyl tin bromide, it being assumed that two molecules of hydroxide combine with one molecule of bromide. The results, including the corrections, are given in Table IV.

TABLE IV

CONDUCTANCE OF 0.0166 N $(CH_3)_3SnBr$ IN ACETONE AT 25° IN THE PRESENCE OF $(CH_3)_3SnOH$

Ratio of hydroxide to bromide	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
Corr. applied $L \times 10^6$	2.07	2.03	1.98	1.94	1.90	1.85	1.81	1.76
Corr. sp. cond. $\times 10^6$	0.0	9.5	18.5	25.8	33.9	39.6	46.2	50.1
Ratio of hydroxide to bromide	0.8	0.9	1.0	1.5	2.0	3.0	5.0	
Corr. applied $L \times 10^6$	1.72	1.67	1.63	1.41	1.2	1.2	1.2	
Corr. sp. cond. $\times 10^6$	56.8	60.6	66.8	88.1	105	131.0	174.0	

The original solution of trimethyl tin bromide had a conductance of 2.07×10^{-6}. On adding only 0.1 mole of hydroxide per mole of bromide, the conductance was raised to 11.8×10^{-6}. The correction due to the conductance of the solvent and to excess bromide was 2.03×10^{-6}, leaving a conductance of 9.5×10^{-6} due to the compound formed between the hydroxide and the bromide. On further addition of the hydroxide, the specific conductance increased, although the rate of increase fell off with increase of total hydroxide added. It may be noted, however, that, on increasing the trimethyl tin hydroxide from two to five moles per mole of bromide, the specific conductance increased from 105×10^{-6} to 174×10^{-6}, or approximately 70%. This indicates that, while a complex electrolyte is formed between the hydroxide and the bromide, it is considerably dissociated in solution. The extent of this dissociation, however, is probably much lower in acetone or in alcohol than it is in naphthalene, as is indicated by the molecular weight in the latter solvent.

The constitution of the complex cation of the dihydroxy bromide cannot be inferred with any degree of certainty from available data. Considering the behavior of trimethyl tin bromide in hydroxy and amino solvents, one might be inclined to ascribe a formula of the oxonium type to the complex cation. Since two molecules of hydroxide are present in the compound, it would then be necessary to consider, either that two oxygen atoms are linked together or that a much more complex structure is involved. For the present, the precise structure of this complex cation must be left open.

The Ditrimethyl Tin Hydroxy Hydroxide, $[(CH_3)_3SnOH]_2 \cdot (CH_3)_3SnOH$.—The experiments described above indicate the existence of a complex cation corresponding to the formula $\{[(CH_3)_3SnOH]_2 \cdot (CH_3)_3Sn)^+$. If such a complex cation exists, we should expect that, on treating the corresponding bromide with silver oxide in aqueous solution, the hydroxide of this ion would be formed. This hydroxide would be isomeric with trimethyl tin hydroxide. In order to determine whether a complex hydroxide is formed under these conditions, the conductance of equivalent solutions of the two hydroxides was compared.

A 0.1 N solution of the complex hydroxide was prepared by treating the corresponding bromide with freshly precipitated silver oxide until the solution gave no test for bromine. The solution was kept in the neighborhood of 0° throughout its preparation. After allowing the precipitated silver bromide to settle, the supernatant solution was siphoned into a cell in which its conductance was measured. If trimethyl tin hydroxide is formed in the above preparation, it would have a concentration of 0.3 N. The specific conductance of a 0.3 N solution of trimethyl tin hydroxide in water at 0 and 25° was found to be 0.890×10^{-4} and 2.03×10^{-4}, respectively, The specific conductance $L \times 10^4$, of the solution of the complex hydroxide, as measured at different times and temperatures, is given in Table V.

TABLE V

CONDUCTANCE OF 0.1 N $(CH_3)_3SnOH_2(CH_3)_3SnOH$ IN WATER

Temp., °C.....	**0**	**0**	**25**	**25**	**29**	**26**	**25**	**25**	**25.05**
Time, hours...	**0**	**12**	**0**	**12**	**24**	**48**	**60**	**72**	**120**
$L \times 10^4$.......	**0.256**	**0.453**	**0.565**	**0.923**	**1.710**	**2.048**	**1.978**	**1.984**	**2.040**

As may be seen from the table, the conductance of the freshly prepared solution of the complex hydroxide is approximately one-fourth that of trimethyl tin hydroxide at the same temperature. Thus, the specific conductance of the freshly prepared solution at 25° was 0.56×10^{-4}, while that of the trimethyl tin hydroxide was 2.03×10^{-4}. The complex hydroxide is not stable. It gradually goes over to trimethyl tin hydroxide, the reaction rate being greatly influenced by the temperature; but even at 0°, the specific conductance increased from 0.26×10^{-4} to 0.45×10^{-4} in a period of twelve hours. Nevertheless, even at 25°, the conversion of the complex hydroxide is not complete until at the end of nearly one hundred hours. At the end of 120 hours, the specific conductance was found to be 2.04×10^{-4} at 25°, while that of a 0.3 N solution of trimethyl tin hydroxide was found to be 2.03×10^{-4}.

The above results show that two moles of trimethyl tin hydroxide combine with one mole of trimethyl tin bromide to form a complex electrolyte in which the bromine is largely ionized. The bromide ion may be replaced by hydroxyl, by treating with silver oxide. The resulting base is a comparatively weak electrolyte, its ionization being about the same as that of trimethyl tin hydroxide at the same molal concentration. It is gradually converted to the normal hydroxide on standing.

Reaction between Trimethyl Tin Hydroxide and Methyl Iodide.—Harada has found evidence that a compound is formed when trimethyl tin hydroxide is treated with methyl iodide in acetone solution.[8]

In order to test this point further, a solution was made up containing 0.1 mole of trimethyl tin hydroxide per liter, and to this was added 0.05 mole of methyl iodide. The conductance of this solution was measured at 25°. The specific conductance of the pure acetone was 1.2×10^{-6} while that of a 0.1 *N* solution of methyl iodide was 1.4×10^{-6} and of the hydroxide, at the same concentration, 5.2×10^{-6}.

Immediately on adding methyl iodide to the solution of trimethyl tin hydroxide, the conductance began to increase and this continued over a considerable period of time. The results are given in Table VI.

The initial values of the conductance rose very rapidly with time. The addition of a large excess of methyl iodide at the end of sixteen hours

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[8] Harada, Thesis, Clark University, 1923.

TABLE VI

CONDUCTANCE OF MIXTURES OF $(CH_3)_3SnOH$ AND CH_3I IN ACETONE

Time, hours	0	0.43	1.0	4.5	13.0	16.0	16.6
$L \times 10^4$	0.184	0.402	0.513	0.987	1.77	2.05	1.86
Time, hours	18.0	20.0	25.8	42.7	49.0	67.0	85.7
$L \times 10^4$	2.51	3.43	4.59	5.42	5.76	6.10	63.1

[a] At this point a large excess of CH_3I was added.

resulted in a marked increase in the rate of reaction, as may be seen from the table. The sum of the conductance due to the components was approximately 0.078×10^{-4}, as against 0.184×10^{-4} for the mixture as initially measured. As time went on, however, the conductance rose. At the end of sixteen hours the specific conductance of the solution had a value approximately twenty-six times that calculated for a mixture of the constituents. At that point, a large excess of methyl iodide was added in order to accelerate the reaction. At the end of eighty-six hours, the solution had reached practically a constant value of 6.31×10^{-4}. Assuming a compound to be formed of the type $[(CH_3)_3SnOH]_2 \cdot CH_3I$, the equivalent conductance of the final solution had a value of 12.6. This value is greater than that of many salts, for example, lithium chloride,[9] lithium nitrate or silver nitrate.[10]

Summary

A convenient method is described for the preparation of the complex dihydroxy bromide, $[(CH_3)_3SnOH]_2 \cdot (CH_3)_3SnBr$. The molecular weight of this compound in naphthalene indicates that it is largely dissociated into its constituents in that solvent.

When the dihydroxy bromide is reduced with sodium in liquid ammonia, some hydrogen is evolved but not enough to correspond to one mole of water in the compound.

Ammino trimethyl tin bromide is precipitated from solutions of the compound in organic solvents. However, the compound is not greatly altered on solution in liquid ammonia.

At higher temperatures the compound is dissociated into its constituents which sublime and recombine. A small proportion of trimethyl tin hydroxide breaks down to dimethyl tin oxide, tetramethyl tin and water under these conditions.

The electrical conductance of the compound in alcohol is approximately twice that of its constituents in the same solvent taken separately.

The conductance of the compound in acetone is much greater than that of its constituents in the same solvent. The conductance of trimethyl tin bromide, on addition of 0.1 mole of hydroxide per mole of

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[9] Sêrkov, J. *Russ. Phys.-Chem. Soc.*, *41*, 9 (1909).

[10] Roshdestwensky and Lewis, J. *Chem. Soc.*, *80*, 2140 (1911).

bromide, is increased thirty times and on addition of two moles, 300 times. On further addition of hydroxide the conductance is further increased, indicating appreciable dissociation of the complex compound in acetone.

On treating the dihydroxy bromide with silver oxide in an aqueous solution, the corresponding hydroxy derivative is obtained. The conductance of the solution clearly indicates that this complex hydroxide has considerable stability. It goes over gradually to trimethyl tin hydroxide, with which it is isomeric.

Trimethyl tin hydroxide forms a complex compound with methyl iodide in acetone. This compound is formed gradually and its solutions are relatively highly ionized. At a concentration of 0.1 N, the equivalent conductance has a value of the order of that of such salts as lithium nitrate and silver nitrate.

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE MECHANISM OF CARBOHYDRATE OXIDATION. XIII. THE ACTION OF POTASSIUM HYDROXIDE ON CALCIUM HEXOSEDIPHOSPHATE. A COMPARISON WITH THAT OF GLUCOSE AND FRUCTOSE[1]

BY WILLIAM LLOYD EVANS AND ROBERT CASAD HOCKETT[2]

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The rates of fermentation of glucose, mannose and fructose are almost the same and the products of these reactions are identical.[3] These facts suggested a fermentation mechanism involving the formation of common intermediates—a condition which seemed easily satisfied on the assumption that these substances were the enediols of the hexoses, especially since no other hexose can yield the same enediols as these, and no other is fermented at a comparable rate. This point of view seemed strengthened through Young's discovery that the same hexosediphosphoric acid[4] ($C_6H_{10}O_4(PO_2(OH)_2)_2$) is formed from each of these three sugars as an intermediate in fermentation as evidenced by the identity, regardless of its source, of all its properties, including optical rotation. Furthermore, this acid has little reducing power except on hydrolysis, and it does not form an osazone without hydrolysis of a phosphate group.

Schlubach and Rauchenberger[5] have recently methylated this common hexosediphosphoric acid and found that only seven methyl groups were

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[1] Read at the Columbus Meeting of the American Chemical Society May, 1929.

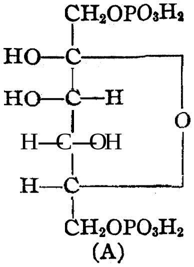
[2] E. I. du Pont de Nemours and Co. Fellow, 1928–1929.

[3] Harden, "Alcoholic Fermentation," Longmans, Green and Co., London. 1923, pp. 32, 48.

[4] Young, Proc. Roy. *Soc.* (London), 81, 528 (1909).

[5] Schlubach and Rauchenberger, *Ber.*, 60B, 1178 (1927).

introduced into the molecule. If this acid were the derivative of an enediol, eight methyl groups should have been present in the resulting compound. The recently proposed structure (A) for this acid[6] easily satisfies the experimental data with reference to the formation of the tetramethyl ester of trimethylhexose-diphosphoric acid.


(A)

By reason of the results obtained in this Laboratory with reference to the action of glucose,[7a] fructose[7b] and mannose[7c] in aqueous solutions of potassium hydroxide, it became of much interest to know the behavior of calcium hexosediphosphate, commercially known as "candiolin," when it was subjected to the same experimental conditions as the three well-known hexose sugars. Especially were we anxious to obtain the experimental data with reference to lactic acid formation. These brief statements summarize our principal objectives in this work.

Experimental Part

Reagents.—The potassium hydroxide, zinc carbonate, phosphoric acid and ether used were of the same degree of purity as the reagents employed with glyceric aldehydes and dihydroxy-acetone.9 The glucose and fructose were Pfanstiehl's c. p. special anhydrous brand with specific rotations recorded, respectively, as +52.5° and −91.66". The calcium hexosediphosphate was presented by the H. A. Metz Laboratories, and was purified before use by the method of Neuberg and Sabatay.[10]

Anal. Subs., 0.900: $Ca_3(PO_4)_2$ by ignition, 0.0411. Calcd. $Ca_3(PO_4)_2$: 45.73. Found: 45.66.

Procedure.—The experimental details were practically the same as in the case of glyceric aldehyde. Glucose and fructose samples of 2.25 g. were used and candiolin samples of 2.827 g. corresponding to 1.125 g. of hexose. The object was to conserve the difficultly prepared material. The three substances were treated as nearly alike as possible.

Products of the Reaction.—The reactions were all carried out at an alkali normality of five and at a temperature of 50°, with time as the variable. Qualitative examination was made for hydroxy acids, acetol, pyruvic acid, formic acid, acetic acid and lactic acid. Quantitative determinations were carried out for the last three named which were the only substances detected.

Data.—The quantitative data are shown in Fig. 1.

Theoretical Discussion and Summary

1. It was found that the yield of lactic acid from glucose in 5 N potassium hydroxide solutions at 50° rises rapidly to a maximum in about

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[6] Levene and Raymond, J. Biol. Chem., 80, 633 (1928); Morgan and Robison, Biochem. J., 22, 1270 (1928); "Annual Survey of American Chemistry," Vol. IV, 1930, p. 256.

[7] (a) Evans, Edgar and Hoff, This Journal, 48, 2665 (1926); (b) Evans and Hutchman, *ibid.*, 50, 1496 (1928); (c) Evans and O'Donnell, ibid., 50, 2543 (1928).

[8] Evans and Hass, ibid., 48, 2763 (1926).

[9] Evans and Cornthwaite, *ibid.*, 50,486 (1928).

[10] Neuberg and Sabatay, Biochena. Z., 151,240 (1925).

twenty-four hours and then remains constant up to at least five hundred and twenty-eight hours. The yields of formic and acetic acids are very low and remain constant over the same range of alkalinity. With fructose the yield of all three acids is greater in amount and constant, at least up to **374** hours. The maximum is reached more rapidly, however, so that in two hours a high yield of lactic acid was obtained. This behavior of fructose seems to be in harmony with the observation that this ketohexose is much more sensitive to some chemical reagents than either glucose or mannose.

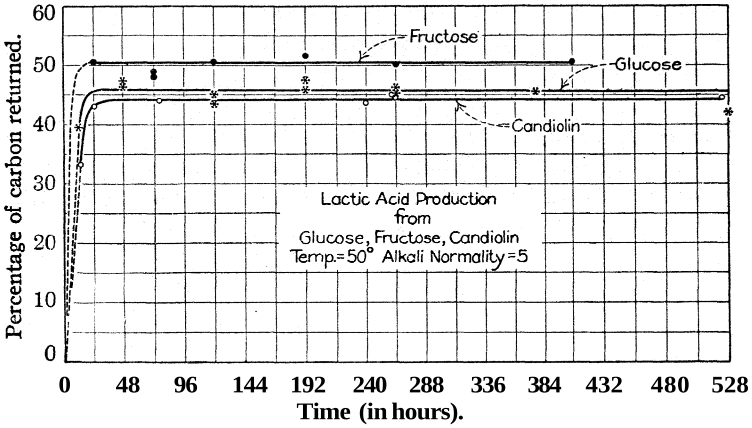

Fig. 1.

2. Candiolin shows a striking similarity in behavior to fructose and glucose. The maximum yield of lactic acid is a little more slowly attained and remains lower than with either of the other compounds, while acetic acid is obtained in larger quantity. It is clear that the rate of hydrolysis of the calcium salt in alkaline solution becomes an important factor in determining the concentration of the resulting hexose. It has been recently pointed out by Shaffer and Friedmann[11] that the yields of products obtained by the action of alkalies on the hexoses are dependent in part on the concentration of the sugar undergoing decomposition. The average yields after attaining a constant production are as follows

	Glucose, %	Fructose. %	Candiolin, %
Lactic	45.55	50.27	44.11
Acetic	0.85	1.52	2.31
Formic	0.47	0 63	0.20
Total	46.87	52.42	46.62

3. From these data and those compared in the diagram, it is clear that the mechanism involved in the formation of lactic, acetic and formic acids in alkaline systems of candiolin is best understood on the basis that

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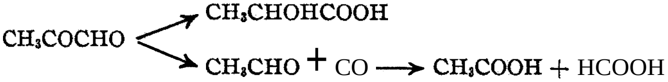
[11] Shaffer and Friedmann, J. *Biol.* Cham., 86, 361 (1930).

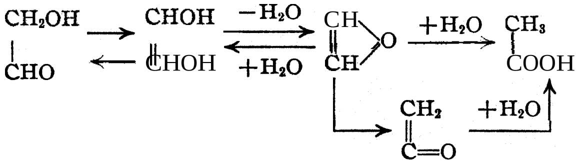
the calcium salt undergoes hydrolysis, thus liberating the keto-hexose, fructose. This sugar is then acted upon by the potassium hydroxide present, thus giving rise both to the sugars formed in the de Bruyn and van Ekenstein[12] interconversion and also to the enediols postulated by Nef.[13] It has been repeatedly pointed out in these studies that lactic acid arises from the hexose-3,4-enediols.

4. It has previously been considered[7"] that acetic and lactic acids, and also a portion of the formic acid obtained in the alkaline decomposition of the sugars are derived from pyruvic aldehyde by a series of reactions which are represented by the equations



$$CH_3COCHO \rightarrow CH_3CHOHCOOH$$
$$CH_3COCHO \rightarrow CH_3CHO + CO \longrightarrow CH_3COOH + HCOOH$$

Formic acid may also be derived from hydroxymethylene formed from the cleavage of hexose-1,2-enediol. From the figures given in paragraph 2, it is seen that the ratios of the yields of acetic and formic acids from glucose and fructose tend to approximate the stoichiometrical relations indicated in the above chemical equations. In the case of candiolin, however, the figures show that the acetic acid is proportionally too great for this equation. Furthermore, it should be pointed out that pyruvic aldehyde osazone has never been obtained in any notable quantity from either glucose, fructose or mannose in 5 N potassium hydroxide solution~.~'At this alkalinity the pyruvic aldehyde intermediate is completely converted into lactic acid. From these facts it follows that an independent source of acetic acid must be postulated. The junior author[14] proposes the following mechanism which is strictly analogous to that suggested by Evans and Benoy[7a] for the formation of lactic acid from glyceric aldehyde.



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[12] De Bruyn and van Ekenstein, *Rec. trav. chim.*, 14, 156 (1895); 14, 203 (1895); 15, 92 (1896); 16, 257 (1897); 16, 274 (1897); 16, 262 (1897); 19, 1 (1900); 27, 1 (1908).

[13] Nef., Ann., 376, 1 (1910); 403, 204 (1914); 357, 294 (1907).

[14] (a) R. C. Hockett, Master's Thesis, The Ohio State University, 1928. Note the analogy between the rearrangement of acetylene oxide into ketene and the well-known rearrangement of ethylene oxide into acetaldehyde. (b) Mr. P. G. Hoff, Doctor's Dissertation, The Ohio State University, 1926, made a similar proposal for the presence of acetic acid in the alkaline decomposition of galactose in which he assumed that glycol aldehyde, through the loss of water, would give rise to ketene, $CH_2=C=O$ as an intermediate, a compound which is known to add water with the formation of acetic acid. This proposal is included as a possibility in the above equations.

The presence of glycol aldehyde is due to the cleavage of the hexose-2,3-enediol or that of a triose-1,2-enediol. It is also conceivable that the formic acid in these reactions may arise from the cleavage of the ethene diol molecule into two molecules of hydroxymethylene.

COLUMBUS, OHIO

[CONTRIBUTION NO. 59 FROM THE MASSACHUSETTS INSTITUTE OR TECHNOLOGY, RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

THE DISSOCIATION PRESSURES OF CERTAIN METAL PYRIDINE THIOCYANATES

BY TENNEY L. DAVIS AND HOWARD R. BATCHELDER

RECEIVED JULY 15, 1930 PUBLISHED OCTOBER 6, 1930

The determination of the dissociation pressures of the compounds of pyridine with metal thiocyanates is part of an investigation of the affinities by which pyridine and similar nitrogen bases are linked in their complex compounds. Of two compounds, such as nickelous tetrapyridine thiocyanate and cobaltous tetrapyridine thiocyanate, for example, which have the same molecular constitution and differ only in the metal which they contain, the one which has the lower dissociation pressure of pyridine is evidently the one in which the pyridine is attached more firmly to the metal. Since the pyridine is supposed to be attached to the coordination valence of the metal, it is to be expected that the order of the metals with reference to their affinity for pyridine will be the same in the series of the salts of one acid as in the series of the salts of another. By comparison, also, of the dissociation pressures of the corresponding pyridine derivatives of different salts of the same metal, it is possible to estimate the effect of the acid radical—for one acid will occupy more or less of the affinity of the metal than another acid and will leave less or more of the affinity available for combination through the coordination valences.

We have worked with cobaltous, cupric, nickelous and zinc pyridine thiocyanates. The compounds were prepared and purified by the methods which had been used earlier for the chloroform-soluble metal pyridine cyanates.[1] Dissociation pressures were measured by starting with a mixture of pyridine with the most highly pyridinated compound of the metal thiocyanate, evacuating the space above it and allowing to come to equilibrium, noting the pressure, then pumping off a small amount of pyridine, again allowing to come to equilibrium and again noting the pressure, and so on, until the pyridine was completely removed from the substance. Thus we were able to be certain that none of the intermediate pyridine complexes escaped us, and that the dissociation pressures of all of the compounds, from that which existed in the presence of an excess

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[1] Davis and Logan, THIS JOURNAL, 50, 2493 (1928).

of pyridine to that which existed in the presence of the non-pyridinated metal thiocyanate, were actually observed.

Cobaltous thiocyanate forms compounds only with two and with four molecules of pyridine, while cobaltous cyanate forms compounds with two, with four and with six molecules—a fact which suggests that the affinity of pyridine for the metal in the thiocyanate series is probably less than in the cyanate series. Studies on the dissociation pressures of the metal pyridine cyanates which are now going on in this Laboratory will throw further light upon the matter.

Description of the Compounds

Cobaltous tetrapyridine thiocyanate[2] separates from chloroform in pink crystals which are moderately soluble in chloroform and more readily soluble in a mixture of chloroform and pyridine. Its solutions in organic solvents undergo the same color changes under the same conditions as solutions of cobaltous hexapyridine cyanate. After a week of exposure to the open air, it is converted entirely into deep blue cobaltous dipyridine thiocyanate.

Cupric dipyridine thiocyanate[3] is a green powder, less soluble in chloroform than the cobalt compound and more readily soluble in chloroform if an excess of pyridine is present. It loses pyridine to form the monopyridine compound, not previously reported, somewhat paler green in color and somewhat less soluble in chloroform than the dipyridine compound. When warmed in a vacuum, it yields black cupric thiocyanate.

Nickelous tetrapyridine thiocyanate[4] crystallizes from chloroform containing an excess of pyridine in blue crystals which resemble crystals of hydrated copper sulfate. When the chloroform solution is distilled or when the crystals are exposed to the air, the substance is converted into a pale blue powder of nickelous dipyridine thiocyanate,[5] sparingly soluble in chloroform. When the tetrapyridine compound is moistened with pyridine, or exposed for a long time to an atmosphere saturated with pyridine, it yields blue-violet crystals of a substance, not heretofore reported, which contains seven molecules of pyridine, possibly nickelous tetrapyridine thiocyanate with three molecules of pyridine of crystallization. The dissociation pressure curve of this substance is parallel to and only slightly lower than the vapor pressure curve of pure pyridine, and is of markedly different slope from those of the other nickelous thiocyanate pyridine complexes.

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[2] Reitzenstein, *Z. anorg. Chem.*, *18*, 253 (1898); 32, 304 (1902); Sand, *Ber.*, 36, 1436 (1903).

[3] Litterscheid, *Arch. Pharm.*, 239, 336 (1901); 240, 74 (1902); Spacu, *Bull. Soc. Stiinte Cluj*, *1*, 284 (1924).

[4] Grossmann, *Ber.*, 37, 559 (1904).

[5] Rosenstein and Cohn, *Z. anorg. Chem.*, 27, 284 (1901).

Zinc tetrapyridine thiocyanate[6] crystallizes in fine white needles from chloroform and pyridine mixture, in which it is moderately soluble. When moistened with pyridine and allowed to stand, it forms a cake of crystals from which the pyridine is removed with difficulty.

TABLE I

ANALYSES

Substance	Metal, %	
	Calcd	Found
Cobaltous monopyridine thiocyanate	23.30	. . .
Cobaltous dipyridine thiocyanate	17.70	17.32, 17.71
Cobaltous tripyridine thiocyanate	14.31	. . .
Cobaltous tetrapyridine thiocyanate	12.00	11.97, 11.92
Cobaltous pentapyridine thiocyanate	10.34	. . .
Cupric monopyridine thiocyanate	24.58	24.92, 25.02
Cupric dipyridine thiocyanate	18.83	18.80
Cupric tripyridine thiocyanate	15.26	. . .
Nickelous monopyridine thiocyanate	23.10	. . .
Nickelous dipyridine thiocyanate	17.62	17.51, 17.35
Nickelous tripyridine thiocyanate	14.24	. . .
Nickelous tetrapyridine thiocyanate	11.95	12.14, 12.04
Nickelous pentapyridine thiocyanate	10.29	. . .
Nickelous hexapyridine thiocyanate	9.04	. . .
Nickelous heptapyridine thiocyanate	8.06	8.46, 8.27
Nickelous octapyridine thiocyanate	7.27	
Zinc tripyridine thiocyanate	15.60	. . .
Zinc tetrapyridine thiocyanate	13.13	13.61, 13.63
Zinc pentapyridine thiocyanate	11.33	

The substances were analyzed for metal—cobalt, nickel and zinc being determined as sulfate, copper as oxide. Results are shown in Table I, where the calculated values for the substances containing one more and one less molecule of pyridine than the found substances are included for comparison.

Measurement of Dissociation Pressures

The apparatus consisted of an ordinary closed-arm manometer mounted on a transparent millimeter scale and sealed to a side-arm, parallel to the arm of the U of the manometer, to the lower extremity of which a 50-cc. Erlenmeyer flask containing a few grams of the substance to be studied had been sealed. As near as practicable beyond this side-arm a tube carrying a glass stopcock was sealed on and inclined upward in such a manner that the Erlenmeyer flask and manometer and side-arm could be immersed completely in the bath while the stopcock remained above the cover of the bath. The apparatus was set up in a 4-liter beaker filled with distilled water, fitted with a tin cover and an electric stirrer, and having an electric light mounted behind it to illuminate the scale. The cover served to prevent excessive evaporation and provided a support from which to suspend the apparatus and the thermometer. Heat was supplied by a micro-burner and, with adequate protection from drafts, it was easy to maintain the temperature constant for several hours within a tenth of a degree. In preliminary ex-

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[6] Grossmann and Hünseler, *Z. anorg. Chem.*, 46, 361 (1905).

periments in which the manometer was outside of the bath, it was found that pyridine distilled into the manometer and that the observed pressure was the vapor pressure of pyridine. The above-described simple apparatus was found to avoid the difficulty. A tube containing phosphorus pentoxide for the absorption of pyridine was inserted between the stopcock and the pump, for it was found that the pyridine, by dissolving in the oil of the pump, otherwise reduced the pump's efficiency.

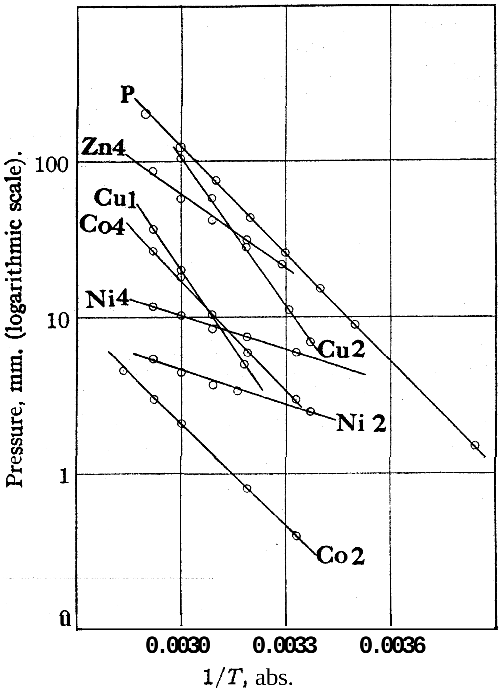


Fig. 1.—Dissociation pressures of metal pyridine thiocyanates. P, pyridine (vapor pressure); Co 4, cobaltous tetrapyridine thiocyanate; Co 2, dipyridine; Cu 2, cupric dipyridine; Cu 1, monopyridine; Ni 4, nickelous tetrapyridine; Ni 2, dipyridine; Zn 4, zinc tetrapyridine.

After the apparatus was assembled, the flask containing the substance having been sealed on, a cubic centimeter or more of pyridine was introduced through the stopcock by means of a capillary dropper, for the purpose of providing enough pyridine to displace all of the air in the system and to insure the presence of the most highly pyridinated compound. The bath was then brought to the desired temperature, the apparatus evacuated, the stopcock closed and readings were taken at intervals until it was apparent that equilibrium had been attained. In each series of experiments, the complete removal of air was confirmed and the accuracy of the apparatus was checked by comparison of the equilibrium pressure when some pyridine was in the flask with the reported vapor pressure of pyridine at that temperature. The pump was then again operated for a short time and a second equilibrium attained checking the first. After this the pump was operated for a longer time, removing pyridine, until it was evident either from a color change or from a sudden decrease in pressure that a change in the substance was taking place. The stopcock was then closed, readings taken as before, and the system again pumped out enough to displace the equilibrium, and so on, until the equilibrium pressure after two successive pumpings was the same. The system was then brought to equilibrium at a different temperature or it was evacuated until the compound of next lower pyridine content began to decompose, and the process was repeated. Observed pressures were corrected to 20° to take account of the expansion of the mercury and glass of the manometer.

The results are conveniently summarized by the chart, Fig. 1, in which the logarithm of the pressure is plotted against the reciprocal of the absolute temperature.

The curves for the dissociation pressures of cobaltous tetra- and dipyridine thiocyanates are practically parallel to each other and to the curve for the vapor pressure of pyridine, which indicates that the affinities of cobaltous dipyridine thiocyanate and of cobaltous thiocyanate for pyridine are practically constant over the temperature range of our observations.

The curves of the cupric compounds approach the pyridine curve at the higher temperatures—and the affinities of cupric thiocyanate and of cupric monopyridine thiocyanate for pyridine decrease with increasing temperature. The curve of cupric dipyridine thiocyanate intersects the pyridine curve at about 70°, at which point the dissociation pressure of the complex and the vapor pressure of pyridine are both equal to 170 mm. Above this temperature the dipyridine compound decomposes spontaneously into cupric monopyridine thiocyanate and pyridine.

The nickelous compounds, on the other hand, show increased affinities for pyridine at the higher temperatures. The curve of nickelous tetrapyridine thiocyanate intersects the pyridine curve at about −3°, and the substance spontaneously decomposes below that temperature. We find that the higher pyridinated compound, when cooled in a freezing mixture, does in fact decompose to produce the lower pyridinated one, but have not been able to measure the vapor pressure at the low temperature.

The affinity of zinc thiocyanate for pyridine decreases with decreasing temperature and disappears at about 20°. A sample of zinc tetrapyridine thiocyanate cooled to −13° showed a pressure of 1.5 mm., which corresponds very closely to the vapor pressure of pyridine at that temperature.

We are not acquainted with any other complex salts which show the remarkable property, exhibited by the nickelous and zinc pyridine thiocyanates, of decomposing when they are cooled.

Reading from the chart, Fig. 1, we get the values for the dissociation pressures at the even temperatures which are shown in Table II.

Table II

Dissociation Pressures (My. of Mercury at 20°)

Temp., °C..........	20	30	40	50	60	70	80
$Co(NCS)_2 \cdot 4Py$	1.9	3.4	6.0	10.6	18.0	27.0	44.0
$Co(NCS)_2 \cdot 2Py$	...	0.5	0.8	1.3	2.1	3.0	4.7
$Cu(NCS)_2 \cdot 2Py$	5.1	12.0	27.0	58.0	106.0	..	..
$Cu(NCS)_2 \cdot Py$	...	3.4	5.0	10.1	20.0	36.0	..
$Ni(NCS)_2 \cdot 4Py$	5.0	6.1	7.5	9.8	10.5	12.0	..
$Ni(NCS)_2 \cdot 2Py$	2.3	2.7	3.3	3.9	4.6	5.2	..
$Zn(NCS)_2 \cdot 4Py$	...	21.5	31.0	42.0	57.0	100.0	..

Summary

The dissociation pressures of cobaltous tetra-and dipyridine thiocyanates, of cupric di- and monopyridine thiocyanates, of nickelous tetra- and dipyridine thiocyanates, and of zinc tetrapyridine thiocyanate have been measured at temperatures between 20 and 80°.

The affinity which holds the pyridine in the cobaltous compounds is practically constant over the temperature range 20 to 80°. In the cupric compounds it decreases at the higher temperatures, while in the nickelous and zinc compounds it decreases at the lower temperatures.

CAMBRIDGE, MASSACHUSETTS

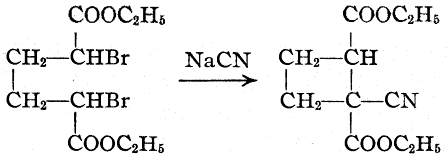
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

RING CLOSURES IN THE CYCLOBUTANE SERIES. II. CYCLIZATION OF α,α'-DIBROMO-ADIPIC ESTERS

BY REYNOLD C. FUSON, OSCAR R. KREIMEIER AND GILBERT L. NIMMO

RECEIVED JULY 17, 1930 PUBLISHED OCTOBER 6, 1930

A new method of effecting the closure of the cyclobutane ring has been reported by Fuson and Kao,[1] who obtained diethyl 1-cyanocyclobutane-1,2-dicarboxylate (I) from diethyl α,α'-dibromo-adipate by treatment with sodium cyanide in absolute alcohol.



I

The method has now been tried with other esters of α,α'-dibromo-adipic acid and of β-methyl-α,α'-dibromo-adipic acid The present article is a report of these experiments.

Since the weight of substituents is known to influence the ease of ring closure, attempts have been made to extend the closure method to α,α'-dibromo-adipic esters in which the alkyl groups were large. For this purpose diphenyl α,α'-dibromo-adipate and di-β-naphthyl α,α'-dibromo-adipate were prepared. The diphenyl ester was prepared from α,α'-dibromo-adipyl chloride by treatment with sodium phenoxide. A somewhat better yield was obtained by heating the acid chloride with phenol. The dinaphthyl ester was prepared by heating α,α'-dibromo-adipyl chloride with β-naphthol.

As was to be expected, these esters could not be studied in ethyl alcohol solutions because of rapid ester interchange. Attempts to replace the absolute alcohol by acetone, ethers, acetonitrile and other solvents led to negative results. Attempts to use other metal cyanides in these solvents were likewise fruitless.

The influence of substituents in the adipic acid chain was then examined. Diethyl α,α'-dibromo-β-methyl adipate (II) was heated for twenty-four hours with powdered sodium cyanide in absolute alcohol.

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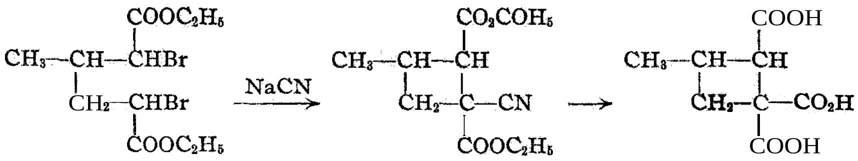
[1] Fuson and Kao, THIS JOURNAL, 51, 1536 (1929).



II III IV

The expected cyano ester (III) was obtained in a yield of 62% of the theoretical. The yield is not quite as high as those obtained with diethyl α,α'-dibromo-adipate (70 to 80%). The position of the cyano group in III has not been determined. The compound is a colorless oil which does not decolorize bromine water or dilute alkaline permanganate solution.

Treatment with a solution of barium hydroxide converted the cyano ester into the methylcyclobutane tricarboxylic acid, IV, which was isolated in the form of the barium salt. Here, of course, the structure was indefinite with respect to one of the carboxyl groups.

Experimental Part

Diphenyl **α,α'-Dibromo-adipate** (from Phenol).—One hundred and forty-six g. (1 mole) of adipic acid was placed in a I-liter flask equipped with a return condenser and 288 g. (2.4 moles) of thionyl chloride was poured in at once. The mixture was warmed gently (50 to 60°) on a water-bath until solution was complete and the evolution of hydrogen chloride had practically ceased. The excess thionyl chloride was then removed by distillation under diminished pressure. The crude adipyl chloride was brominated by adding 367.5 g. (2.3 moles) of dry bromine and 10 g. of phosphorus tribromide and heating at 50 to 60° for thirty-six to forty-eight hours under a strong light.

To the crude α,α'-dibromo-adipyl chloride was added 188 g. (2 moles) of phenol. The mixture was maintained at a temperature of 50 to 60° for twenty-four hours. To the reaction mixture was then added 500 cc. of benzene; the solution obtained by heating this mixture was cooled and the ester separated in crystalline form. Treatment with charcoal removed the dark color from the benzene solution and the ester was obtained after one additional recrystallization from benzene as colorless crystals melting at 146–148". The yield was 83 g. or 18.4% of the theoretical.

Anal. Calcd. for $C_{18}H_{16}O_4Br_2$: Br, 35.1. Found: Br, 34.7.

Diphenyl **α,α'-Dibromo-adipate** (from Sodium Phenoxide).—The ester was made also by treating one mole of the crude α,α'-dibromo-adipyl chloride with 232 g. (2 moles) of sodium phenoxide. The chloride was placed in an ice-bath and the sodium phenoxide was added gradually in small portions. Small amounts of benzene (200 cc. in all) were added from time to time and the reactants were thoroughly mixed by shaking. The ester was removed by extracting the solid mass with 800 cc. of boiling benzene. By concentration of the benzene extracts, 31.5 g. of the ester was obtained in nearly pure form. This corresponds to a yield of 7% of the theoretical.

Di-β-naphthyl α,α'-Dibromo-adipate.—To the dibromo-adipyl chloride obtained from one-half mole of adipic acid was added in portions one mole of β-naphthol. The mixture was stirred vigorously during the addition and after being dissolved in 200 to 300 cc. of benzene was allowed to stand. The crude ester which separated after several hours was recrystallized from acetone. It melted at 165–166.8°. The yield was 28.5 g. or 10% of the theoretical.

Anal. Calcd. for $C_{26}H_{20}O_4Br_2$: Br, 28.7. Found: 28.4.

Diethyl 3-Methyl-1-(or 2)-cyano-1,2-cyclobutane Dicarboxylate.—Eight g. of powdered sodium cyanide was placed in a 200-cc. round-bottomed flask containing a solution of 20 g. of diethyl α,α'-dibromo-β-methyl adipate in 15 cc. of absolute alcohol. The mixture was heated under reflux on the steam-bath for twenty-four hours. It was then cooled and filtered by means of suction to remove solid inorganic substances (sodium bromide and excess sodium cyanide). The solid material was washed with ether and the washings were added to the filtrate, which after the removal of the ether and alcohol boiled at 140 to 143° at 3 mm. The yield of diethyl 3-methyl-1-(or 2)-cyano-1.2-cyclobutane dicarboxylate was 8 g. or 63% of the theoretical; d_4^{20} 1.08854; n_D^{21} 1.44735.

Anal. Calcd. for $C_{12}H_{17}O_4N$: C, 60.2; H, 7.2. Found: C, 59.7; H, 7.2.

Hydrolysis of the Cyano Ester.—The cyano ester was hydrolyzed by treatment with hot barium hydroxide (20%) according to the method of Perkin.[2] From 8 g. of the ester was obtained 8.5 g. of the barium salt of the tricarboxylic acid; this corresponds to a yield of 67% of the theoretical.

Anal. Calcd. for $C_{16}H_{14}O_{12}Ba_3$: Ba, 50.8. Found: Ba, 50.9.

Summary

Diethyl α,α'-dibromo-β-methyl adipate has been converted by treatment with sodium cyanide in absolute alcohol into diethyl 3-methyl-1-(or 2)-cyano-1,2-cyclobutane dicarboxylate. The latter has been hydrolyzed to the corresponding cyclobutanetricarboxylic acid, which has been isolated in the form of its neutral barium salt.

The diphenyl and di-β-naphthyl esters of α,α'-dibromo-adipic acid have been prepared. Attempts at ring closure were unsuccessful with these esters.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE]

THE SYNTHESIS OF SOME NEW COMPOUNDS RELATED TO APOCYNIN AND APOCYNOL[1]

BY HENRY P. HOWELLS, B. H. LITTLE AND H. P. ANDERSEN

RECEIVED JULY 19, 1930 PUBLISHED OCTOBER 6, 1930

The syntheses described herein were undertaken originally with the aim of securing intermediates for a study of the effect of length of side chain upon the physiological properties of certain unstudied phenolic bodies related to guaiacol. In choosing the method of preparation for such intermediates as the acyl substituted guaiacols, the findings of Finnemore[2] on methods of obtaining acetovanillone appeared to answer our immediate problem. His work[3] suggested also new lines of thought that made the

[2] Perkin, J. *Chem. Soc.*, *65*, 580 (1894).

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[1] This communication is an abstract of portions of theses submitted by B. H. Little and H. P. Andersen in partial fulfilment of the requirements for the degree of Master of Science at the Oklahoma Agricultural and Mechanical College.

[2] Finnemore, J. *Chem. Soc.*, 93, 1520 (1908).

[3] Finnemore[2] pointed out that apocynol or α-(4-hydroxy-3-methoxyphenyl)-methyl carbinol and its demethylated product possessed certain structural similarities to epinephrine, and stated that these products were still under investigation since the

synthesis of our products seem even more interesting in a study of the relation of structure to physiological action.

Apocynin, a constituent of the extract from Canadian Hemp (*Apocynum cannabinum*) used in medicine mainly as a cardiac stimulant and a diuretic, was shown by Finnemore[4] to be identical with acetovanilloneor (4-hydroxy-3-methoxyphenyl) methyl ketone. In order to obtain the latter substance in sufficient amounts for further study, a new synthesis[2] was devised in which apocynol, resulting from the hydrolysis of the product obtained by the action of vanillin benzoate with the Grignard reagent, was oxidized with a chromic acid mixture. The carbinol could not be obtained directly by reacting vanillin with methylmagnesium iodide. In the present work this reaction also failed to go when other alkylmagnesium halides were used with vanillin.

It was hoped that the above method for obtaining the benzoate of apocynol could be adapted here in the preparation of its ethyl, n-propyl, *n*-butyl and n-amyl homologs, which might serve as starting materials. These compounds would yield the desired homologs of apocynol and apocynin when subjected to suitable oxidation and hydrolytic changes. Such changes have been carried out with greatest success in the case of the n-butyl derivatives by modifying the work of Finnemore for similar transformations. The various modifications will be described in detail later, but two of the more important changes should be pointed out here. First, it was found essential to use molecular quantities in reacting vanillin benzoate with the Grignard reagent to form the a-(4-benzoxy-3-methoxyphenyl)-*n*-alkyl carbinols. This was accomplished through the use of the titration method of Gilman[5] and co-workers for determining R-Mg-X in the reagent. Second, alcoholic potassium hydroxide was used to hydrolyze the benzoate esters in place of aqueous potassium hydroxide as used by Finnemore in forming apocynol. The factor which necessitated this change was no doubt due to the decreased solubility in water of the higher molecular weight esters. Absolute alcohol possessed a marked advantage over water as a solvent in diminishing greatly the time required for the reaction and the degree of decomposition of the hydrolyzed product in the hot alkaline solution. Since the n-butyl members of the above groups of compounds were much more easily prepared than the n-propyl and n-amyl members of each series, and since the five carbon side chain appeared to be of sufficient length for representative pharmacological testing, only the work with the n-butyl compounds has been described in detail in this paper.

physiological properties promised to be of interest. Through private communication it was learned that he did not extend this work.

[4] Finnemore, J. *Chem. Soc.*, 93, 1513 (1908).

[5] Gilman, Zoellner and Dickey, THIS JOURNAL, 51,1576 (1929).

The faint vanillin-like odor of apocynin noted by Finnemore[2] suggested to us at the start that the present study might lead to some interesting observations of the relation between chemical constitution and odor. It was observed also that Nomura and co-workers had made in recent years a series of studies with homologs of zingerone and related compounds with the view of unraveling the relation between their chemical constitution and pungency. In one of the earlier papers[6] it was found that 4-hydroxy-3-methoxyphenylbutane, possessed a pungent taste similar to zingerone. Thus it appeared that the presence of the carbonyl group in the side chain of zingerone is not essential, although it did seem to produce some effect on the taste. In view of the latter fact, the isomeric ketones which are prepared in the progress of this work may be of additional value in a study of the effect on taste or odor produced by the shifting of the carbonyl group in the side chain. The work has not been sufficiently advanced to draw conclusions but the odor and taste of certain products described herein at least indicate that some interesting correlations along this line may be possible.

Experimental

Benzoate of Vanillin.—The method used by Popovici[7] for the preparation of this compound was modified as follows. To a solution of 50 g. of vanillin in 125 cc. of 10% sodium hydroxide there was added rapidly and with vigorous shaking 46 cc. of benzoyl chloride, cooling intermittently so as to allow the benzoate ester to crystallize out in small white globules. Excess benzoyl chloride was decomposed by addition of 50 cc. of 10% sodium hydroxide and shaking well. The precipitate was collected, washed with 2 *N* ammonium hydroxide followed by slightly warmed water, dried and crystallized from 75% alcohol, when it appeared as colorless, monoclinic needles, m. p. 77" (corr.); yield, about 78%. Popovici reported the m. p. as 78° and Worner[8] gave 75°.

α-(4-Benzoxy-3-methoxyphenyl)-*n*-butyl carbinol, $C_6H_3(OCOC_6H_5)(OCH_3)$-**$(CHOHC_4H_9)$.—This** compound was prepared by a method somewhat similar to that used by **Finnemore**[2] for obtaining the simpler methyl carbinol by the action of the Grignard reagent upon the benzoate of vanillin. The present Grignard reagent was prepared essentially by the method recommended recently by Gilman[6] and co-workers, using 37 g. of *n*-butyl iodide, 4.8 g. of magnesium, a small crystal of iodine and 10 cc. of anhydrous ether in a closed system. The titration method of Gilman and co-workers for estimating n-butylmagnesium iodide showed the yield of reagent to be about 70% in most of the runs. The diluted Grignard reagent was cooled with an ice-bath and to it was added dropwise with constant stirring 35 g. of vanillin benzoate dissolved in slightly warmed anhydrous ether. The mixture was stirred for three hours and then boiled gently for half an hour, after which it was cooled and decomposed with cracked ice and 2 *N* sulfuric acid. The ether layer was washed with a saturated sodium bisulfite solution. 1.0% sodium hydroxide, and water in the order named The ether solution was saturated with carbon dioxide. dried over anhydrous sodium sulfate, filtered and evaporated under diminished pressure on a water-bath. A colorless oil remained which solidified largely upon cooling. The oily solid was washed with ligroin (b. p 90–120°)

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[6] Nomura and Hotta, *Sci. Repts. Tôhoku Imp. Univ.*, 14, 119 (192.5).

[7] Popovici, *Ber.*, 40, 3504 (1907).

[8] Wörner, *ibid.*, 29, 139 (1896).

and crystallized from 75% alcohol, when it appeared as colorless monoclinic needles, m. p. 109.3° (corr.); yield, about 48%.

Ad. Calcd. for $C_{19}H_{22}O_4$: C, 72.61; H, 7.06. Found: C, 73.05; H, 7.20.

The compound was soluble in alcohol, acetone, ether and glacial acetic acid, but insoluble in water. The crystals dissolved in cancentrated sulfuric acid to give a red color, but dilute alcoholic ferric chloride gave no change.

α-(4-Hydroxy-3-methoxyphenyl)-*n*-butyl carbinol, $C_6H_3(OH)(OCH_3)(CHOHC_4H_9)$, was obtained by the hydrolysis of the above benzoate ester through a modification of the method used by Finnemore[2] for preparing the simpler homolog, apocynol. A solution of 3 g. of the benzoate in 50 cc. of 10% alcoholic potassium hydroxide was refluxed for thirty minutes. The alcohol was evaporated off under suction and the residue was dissolved in water. The solution was saturated with carbon dioxide and the precipitate which settled out was taken up in ether. The ether solution was dried over anhydrous sodium sulfate and then evaporated to a brown solid residue mixed with some oily impurity. The oil was insoluble in boiling ligroin (b. p. 90–120°) but the solid material dissolved and separated out upon cooling as colorless monoclinic crystals, m. p. 81.5° (corr.); yield, about 10%.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.57; H, 8.57. Found: C, 68.10; H, 8.82.

The crystals dissolved in concentrated sulfuric acid to give a red color, and in dilute alcoholic ferric chloride to form a blue color. The product was soluble in alcohol, acetone, chloroform, ethyl acetate and dilute sodium hydroxide. The product possessed a very faint clove-like odor.

(4-Benzoxy-3-methoxyphenyl)-*n*-butyl ketone, $C_6H_3(OCOC_6H_5)(OCH_3)(COC_4H_9)$.—The corresponding carbinol was oxidized to the ketone derivative in essentially the same manner as described by Bogert and Howells[9] for the oxidation of acyl hydroquinones to the corresponding quinones. A solution of 10 g. of the carbinol in 50 cc. of warm glacial acetic acid was added slowly (ten minutes) to a mixture of 10 g. of potassium dichromate, 10 cc. of concentrated sulfuric acid and 100 cc. of water, while the solution was stirred vigorously. This stirring was continued for about ten minutes after all of the carbinol had been added, during which time the temperature was brought to about 85°, and then cooled. The mixture was diluted with an equal volume of water and, after a short period of standing, the precipitate was filtered off, washed well with water and dried. Recrystallized from alcohol, it gave colorless, shiny triclinic crystals, m. p. 88.1° (corr.) yield, about 92%.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.08; H, 6.39. Found: C, 72.87; H, 6.42.

The product was soluble in ether, acetone and chloroform, but insoluble in dilute sodium hydroxide. The crystals dissolved in concentrated sulfuric acid to give a yellow color. The product possessed no particular odor.

The phenylhydrazone when crystallized from alcohol gave colorless triclinic crystals, m. p. 163' (corr.); yield, about 46.5%. The crystals dissolved in concentrated sulfuric acid to give a yellow color. Nitrogen was determined by Milbauer's[10] modification of the Kieldahl method.

Anal. Calcd. for $C_{25}H_{26}O_3N_2$: N, 6.96. Found: N, 6.94.

(4-Hydroxy-3-methoxyphenyl)-*n*-butyl ketone, $C_6H_3(OH)(OCH_3)(COC_4H_9)$, was obtained by the hydrolysis of the above benzoate ester, using the same method already described for the corresponding carbinol derivative. The solid residue which remained after evaporating off the ether was recrystallized from 25% alcohol. A mixture of color-

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[9] Bogert and Howells, THIS JOURNAL, 52, 837 (1930).

[10] Milbauer, *Z. anal.* Chem., 42, 725 (1903).

less monoclinic and triclinic crystals seemed to separate out, m. p. 62.9° (corr.); yield, about 90%.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.23; H, 7.69. Found: C, 68.95; H, 7.68.

The ketone did not possess the faint vanillin odor characteristic of the lower homolog, acetovanillone (apocynin), but it did carry a very faint pleasant odor. The product was soluble in alcohol, acetone, chloroform, ethyl acetate, hot benzene and toluene, and slightly soluble in hot water. The crystals dissolved in concentrated sulfuric acid to give a yellow color, and in dilute alcoholic ferric chloride to form a greenish-yellow color. The ketone was apparently decomposed by boiling 50% sulfuric acid with the evolution of products having a faint guaiacol odor mixed with a penetrating odor characteristic of some of the lower fatty aldehydes. The remaining solution turned a greenish-yellow color unlike the red color noted by Finnemore[2] in the case of apocynin.

Attempts were made to prepare the phenylhydrazone, β-naphthylhydrazone and *p*-nitrophenylhydrazone, but the products were all oils which were too difficult to purify. The semicarbazone seemed to form, but physical examination and color reaction pointed to it as being the starting material.

The diphenyl urethan was formed from diphenylcarbamine chloride in the usual manner. The product gave fluffy needles from alcohol, m. p. 121.5–123° (corr.); yield, about 52%.

Anal. Calcd. for $C_{25}H_{25}O_4N$: N, 3.47. Found: N, 3.30.

Comparative Yields of Carbinols from Vanillin Benzoate with Some Grignard Reagents.—In view of the findings of Gilman[6] and co-workers, that the even-numbered halides give yields of Grignard reagents higher than the preceding halides that have an odd number of carbon atoms and furthermore a gradual drop in yield results in a given series with the ascent of that series to halides of higher molecular weight, it might be expected that n-butylmagnesium bromide would give a better yield of the carbinol than that from n-propyl- or n-amylmagnesium bromide in the usual mode of synthesis. However, the relative yields obtained in this work cannot be accounted for in this way, since the titration method of Gilman and co-workers was used in correcting for molecular proportions of reagents. It was also found that n-butyl iodide gave better results than n-butyl bromide when used in the synthesis of the carbinol, although we had predicted greater success with the bromide, since the above workers found that with a given alkyl group the lower yields are with iodide and the higher with the bromide. Perhaps n-butylmagnesium bromide is too active and not only attacks the aldehyde part of vanillin benzoate but also reacts with the phenyl ester group giving rise to oily by-products. Recent work[11] on the relative reactivities of some Grignard reagents indicates butylmagnesium bromide to be much more reactive than the iodide. Further work is being done in this connection to determine the relative merits of R-Mg-I and R-Mg-Br in reactions of the above type.

α-(4-Benzoxy-3-methoxyphenyl)-*n*-propyl carbinol, $C_6H_3(OCOC_6H_5)(OCH_3)(CHOHC_3H_7)$, was obtained by essentially the same method that was described for the

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[11] Gilman, Heck and St. John, *Rec. trav. chim.*, 49, 212 (1930).

n-butyl homolog. Colorless monoclinic crystals formed upon recrystallization from alcohol, m. p. 111.3° (corr.); yield, about 31.5%.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 72.00; H, 6.67. Found: C, 71.61; H, 6.90.

The crystals were soluble in ether, chloroform and glacial acetic acid, but insoluble in water. The product dissolved in concentrated sulfuric acid to give a red color. The compound possessed a faint pleasant odor.

(4-Benzoxy-3-methoxyphenyl)-*n*-propyl ketone, $C_6H_3(OCOC_6H_5)(OCH_3)(COC_3H_7)$.—The above carbinol was oxidized readily by the method already described for the n-butyl homolog. Colorless triclinic crystals were obtained from alcohol, m. p. 79° (corr.); yield, about 51.5%.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.48; H, 6.04. Found: C, 71.82; H, 6.00.

The crystals were soluble in ether, acetone and chloroform, but insoluble in dilute alkali. The product dissolved in concentrated sulfuric acid to give a yellow color.

The phenylhydrazone when crystallized from alcohol gave colorless triclinic crystals, m. p. 175.5° (corr.). The crystals dissolved in concentrated sulfuric acid to give a yellow color.

Anal. Calcd. for $C_{24}H_{24}O_3N_2$: N, 7.22. Found: N, 7.12.

α-(4-Benzoxy-3-methoxyphenyl)-*n*-amyl carbinol, $C_6H_3(OCOC_6H_5)(OCH_3)(CHOHC_5H_{11})$, was also obtained by essentially the same method as described for its n-butyl homolog. The crude product was an oil mixed with about an equal amount of solid material, which was finally purified after considerable difficulty. Most of the oil was eliminated by pressing the crude product on a porous plate and allowing it to stand for several hours in a refrigerator. The mixture had a pleasant pungent odor along with a marked odor resembling that of valeric acid. The product was finally washed with ligroin and recrystallized from alcohol as colorless monoclinic crystals, m. p. 95.6° (corr). The yield varied widely and usually resulted a bit below 10%, although one run seemed to give close to a 48% yield of a product which melted only a few degrees from the correct melting point.

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.17; H, 7.32. Found: C, 72.91; H, 7.95.

The crystals were soluble in ether, chloroform, acetic acid and ethyl acetate, but insoluble in water. The product dissolved in concentrated sulfuric acid to give a red color.

The carbinol was oxidized with a chromic acid mixture for producing the ketone derivatives but the small amount of liquid product could not be sufficiently purified for complete identification. The small quantity of oil was apparently changed readily to the phenylhydrazone in the usual manner. The product after one crystallization from 75% alcohol gave colorless crystals, m. p. 134.6" (corr.). The crystals dissolved in concentrated sulfuric acid to give a yellow color.

Anal. Calcd. for $C_{26}H_{28}O_3N_2$: N, 6.73. Found: N, 6.65.

Summary

1. Some new derivatives of the n-propyl, n-butyl and *n*-amyl homologs of apocynol and apocynin have been prepared and described. The n-butyl derivatives are apparently the most readily obtained of the series and thus have been studied in detail to give the n-butyl homologs of apocynol and apocynin, which appear to be of interest in a study of the relation between structure and physiological action.

2. Tests on the comparative yields of the carbinols from vanillin benzoate and the Grignard reagent seem to indicate that R-Mg-I reagents are

superior to the R-Mg-Br type. Further work is being planned to determine the relative merits of the iodides and bromides in reactions of the above type.

STILLWATER, OKLAHOMA

[CONTRIBUTION NO. 61 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

STUDIES IN THE DIPHENIC ACID AND PHTHALIC ACID SERIES. IV

BY H. W. UNDERWOOD, JR., AND G. E. BARKER[1]

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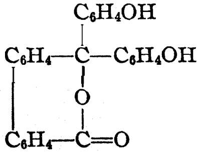
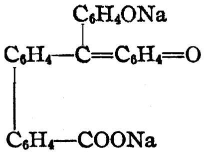
I. The Structure of Phenoldiphenein

Phenoldiphenein dissolves in sodium hydroxide solution with the development of a light yellow color.[2] The apparently anomalous behavior of this compound makes it desirable to obtain evidence regarding its structure. The arrangement of the groups in phenolphthalein has been established by the isolation of *p,p'*-dihydroxybenzophenone and benzoic acid from the melt obtained by the fusion of the phthalein with potassium hydroxide. The analysis of the potassium salt of phenolphthalein and the preparation of a dimethyl ether show the presence of two acidic hydrogen atoms and two hydroxyl groups. An account of the application of these procedures to phenoldiphenein is given in this paper. The results of our experiments show that phenoldiphenein and its sodium salt are represented by the formulas



$$\begin{array}{lcl} & C_6H_4OH & \\ & | & \\ C_6H_4- & C & -C_6H_4OH \\ | & | & \\ | & O & \\ | & | & \\ C_6H_4- & C & =O \end{array}$$

and



$$\begin{array}{lcl} & C_6H_4ONa & \\ & | & \\ C_6H_4- & C & =C_6H_4=O \\ | & & \\ | & & \\ C_6H_4- & COONa & \end{array}$$

Apparently the groups in diphenic anhydride give a light yellow instead of a red color to the sodium salt of the phenol condensation product.

Discussion of Experiments

All of the temperatures given are uncorrected.

Fusions of Phenolphthalein, Phenoldiphenein and the Fluorenone-phenol Condensation Product with Potassium Hydroxide.—A procedure which gave satisfactory results with phenolphthalein was first developed, and this was applied to phenoldiphenein and the fluorenone–phenol condensation product.

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[1] Some of the experimental results described in this paper are taken from a thesis submitted to the Faculty of the Massachusetts Institute of Technology by G. E. Barker in partial fulfilment of the requirements for the degree of Bachelor of Science.

[2] Underwood and Kochmann, THIS JOURNAL, 45, 3071 (1923); 46, 2069 (1924).

An intimate mixture of 5 g. of powdered phenolphthalein (0.016 mole) and 20 g. of powdered potassium hydroxide (0.357 mole) was placed in a 60-cc. nickel crucible, and heated over a free flame until the solid melted. The crucible was allowed to cool while its contents were thoroughly stirred. The product was transferred to a mortar, ground to a fine powder and then placed in the crucible. After the mixture had been heated to its melting point, it was cooled, transferred to a mortar and reduced to a powder. The product was fused a third time, Since a solution of a sample of the mixture in water was not red, it was concluded that all of the phenolphthalein had been decomposed. The melt was extracted with four 50-cc. portions of boiling water and the solution was acidified with hydrochloric acid. The precipitate was collected on a filter, dried in the air and ground in a mortar with two 25-cc. portions of chloroform. Evaporation of the filtered chloroform extracts to dryness gave a colorless solid; this was crystallized from 15 cc. of boiling water. The product, which weighed 0.84 g. (43.8% yield) and melted at 119–120°, was identified as benzoic acid. The material which did not dissolve in chloroform was crystallized twice from 15 cc. of boiling water. About 1 1 g. (32.7% yield) of *p,p'*-dihydroxybenzophenone, m. p. 206–207°, was obtained.

The procedure described above was employed in the fusion of 3 g. of phenoldiphenein (0.0076 mole) with 9.6 g. of potassium hydroxide (0.1711 mole). During the fusion a white vapor which had an odor like that of biphenyl was evolved, and the mixture was black after a third fusion. Acidification of the filtered solution of the melt caused the evolution of considerable carbon dioxide and the formation of a dark colored gelatinous precipitate. The solid was collected on a filter, dried and extracted with four 10-cc. portions of boiling benzene. Evaporation of the benzene solutions to dryness gave a light gray solid which weighed 0.5 g. (33% yield) and melted at 110–111° after crystallization from a small amount of an alcohol–water mixture. The material dissolved in concd. sulfuric acid with the development of a wine-red color. The properties of this substance indicated that it was o-phenylbenzoic acid. Addition of an excess of bromine water to the filtrate from the gelatinous precipitate gave a colorless solid; this was filtered and dried in the air. The material, which weighed 1.22 g. and melted at 95°, was identified as *sym.*-tribromophenol; the product is equivalent to 0.347 g. of phenol (24.3% yield). Apparently phenoldiphenein is transformed into salts of phenol, o-phenylbenzoic acid and carbon dioxide by fusion with potassium hydroxide.

Similarly we secured 0.79 g. of *sym.*-tribromophenol (13.95% yield) and about 0.1 g. of o-phenylbenzoic acid (6% yield) from the melt obtained by fusing 3 g. of the fluorenone-phenol condensation product (0.0086 mole) with 7 g. of potassium hydroxide (0.1247 mole).

Analysis of the Potassium Salts of Phenolphthalein and Phenoldiphenein.—Procedures which gave satisfactory results with phenolphthalein were first developed, and these were applied to phenoldiphenein.

A solution of 0.5 g. of potassium hydroxide in 18 cc. of distilled water was thoroughly shaken with 1.49 g. of powdered phenolphthalein (calcd. amt. X 1.05) for twenty minutes and filtered. The filtrate was evaporated to dryness in a large dish; the dark red potassium salt was dried at 160° for four hours and cooled in a desiccator over concd. sulfuric acid.

Two-tenths gram of the dry potassium salt of phenolphthalein was placed in a weighed platinum crucible, and the latter was inclined on its side on a nichrome wire triangle. After three drops of pure, concd. sulfuric acid had been added to the salt, a platinum cover was placed on the crucible and the latter was carefully heated for about two and one-half hours at a temperature just below visible redness. At the end of this period the ash was practically colorless. A lump of pure ammonium carbonate about the size of a pea was introduced, and the mixture was heated to dull redness for half an hour.

The crucible was now allowed to cool to room temperature in a desiccator containing anhydrous calcium chloride, weighed, heated again and reweighed. This procedure was repeated until the weight of the crucible was constant. From the quantity of colorless potassium sulfate in the crucible the percentage of potassium in the salt was calculated.

Anal. Calcd. for $C_{20}H_{12}O_4K_2$: K, 19.83. Found: K, 19.88, 19.81.

The procedures described above were used for the preparation and analysis of the potassium salt of phenoldiphenein. This salt is an amorphous greenish-yellow powder; its color is between shade 1 of yellow and the normal tone of greenish-yellow in Mulliken's color charts.[8] A very dilute solution of the sodium salt of phenoldiphenein becomes practically colorless upon the addition of a large excess of concd. sodium hydroxide solution.

Anal. Calcd. for $C_{26}H_{16}O_4K_2$: K, 16.62. Found: K, 16.67. 16.61.

Lactone Dimethyl Ethers of Phenolphthalein and Phenoldiphenein.—Procedures which gave satisfactory results with phenolphthalein were first developed, and these were applied to phenoldiphenein.

A solution of 6 g. of phenolphthalein, 18 g. of methyl iodide (calcd. amt. X 3.36) and 0.6 g. of powdered potassium hydroxide in 40 cc. of methyl alcohol was maintained at 40–45° for twenty-four hours, and then 0.6 g. of powdered potassium hydroxide was added. At intervals of twenty-four hours another 0.6-g. and a 0.4-g. portion of powdered potassium hydroxide were introduced, and the mixture was kept at 40–45° during this period and for twenty hours after the last addition of alkali. The product was transferred to a beaker which was left in a vacuum desiccator over anhydrous calcium chloride until the solvent evaporated. The dry residue was placed in a beaker, stirred with 50 cc. of water, collected on a filter, washed with two 20-cc. portions of 5% potassium hydroxide solution and with 20 cc. of water and dried. The yield of phenolphthalein lactone dimethyl ether, m. p. 100–101°, was 5.68 g. (87%).

By use of the procedure described above, we secured 1.6 g. of crystalline lactone dimethyl ether of phenoldiphenein (50% yield) from 3 g. of phenoldiphenein, 7.26 g. of methyl iodide (calcd. amt. × 3.36) and 0.9 g of powdered potassium hydroxide (calcd. amt. × 1.05), added in three portions of 0.25 g. and one of 0.15 g. Thirty-five cc. of methyl alcohol was used as a solvent. Phenoldiphenein lactone dimethyl ether was obtained in the form of colorless stout needles, m. p. 150–151°, by crystallization from a small amount of methyl alcohol. The compound is insoluble in 10% sodium hydroxide solution.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.59; H, 5.25. Found: C, 79.36, 79.56; H, 5.61, 5.58.

Forty grams of active, anhydrous aluminum chloride was added, with stirring, to 40 g. of dry phthalic anhydride and 50 g. of dry anisole (calcd. amt. X 0.855). After a reflux water condenser fitted with a drying tube containing anhydrous calcium chloride had been attached to the flask, the mixture was allowed to stand overnight at room temperature and then heated for three hours on a water-bath. The contents of the flask were diluted with 200 cc. of water and heated for an hour on a water-bath. The product was transferred to a beaker, and 50% sodium carbonate solution was added until the mixture was neutral. The solid was collected on a filter, ground in a mortar with two 50-cc. portions of 50% sodium carbonate solution and then with 50 cc. of 6 *N* potassium hydroxide solution. The material was collected on a filter again, washed with 50 cc. of water, dried and extracted with two 200-cc. portions of boiling methyl

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[8] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, 1904, Vol. I.

alcohol. The filtered methyl alcohol solution was concentrated and cooled in ice to facilitate the crystallization of the phenolphthalein lactone dimethyl ether. The product weighed 28 g. (35% yield) and melted at 100–101°.

By use of the procedure described above, we obtained 0.76 g. (11.1% yield) of crystalline lactone dimethyl ether of phenoldiphenein, m. p., 150–151°, from 5 g. of dry diphenic anhydride, 3.5 g. of dry anisole (calcd. amt. × 0.725) and 3.1 g. of active, anhydrous aluminum chloride. Fifty cc. of water was used to dilute the reaction mixture. The solid reaction product was washed successively with 15 cc. each of 50% sodium carbonate solution, 6 *N* potassium hydroxide solution and water. The dry material was extracted with two 50-cc. portions of boiling methyl alcohol.

II. Reactions of Derivatives of Diphenic Acid and Phthalic Acid with Acetic Anhydride

When the monomethyl, mono-ethyl, dimethyl and diethyl esters of diphenic acid were heated with acetic anhydride, each compound remained unchanged. Under similar conditions diphenamic acid was dehydrated in two different ways, giving diphenimide and 1-cyanobiphenyl-10-carboxylic acid; the diamide of diphenic acid was transformed into 2,2′-dicyanobiphenyl. These reactions are dehydrations and involve union of the side chains attached to the rings.[4] Since our investigations involve a comparison of the behavior of derivatives of diphenic acid and those of phthalic acid, we have studied the action of acetic anhydride upon the methyl and ethyl esters, the mono-amide and the diamide of phthalic acid.

Discussion of Experiments

Monomethyl Phthalate.—After a mixture of 25 g. of phthalic anhydride and 125 g. of absolute methyl alcohol (calcd. amt. × 23.1) had been refluxed on a water-bath for five hours, the excess methanol was distilled and the reaction product transferred to a beaker which was left in a desiccator over anhydrous calcium chloride for several hours. The yield of monomethyl phthalate, m. p. 82–82.5°, was 24.4 g. (80.2%).

Ten grams of the ester was heated with 20 g. of glacial acetic acid and 30 g. of acetic anhydride for sixteen hours at 145°. The mixture was cooled in ice and the solid which formed was collected on a filter and dried. The filtrate was concentrated by distillation at 145° and the residue was transferred to a beaker, cooled and dried. The solid reaction product, which weighed 8.1 g. (98.5% yield), was identified as phthalic anhydride. Two cc. of impure methyl acetate was obtained by several fractionations of the distillate. Three and nine-tenths grams of phthalic anhydride was secured by heating 10 g. of monomethyl phthalate for sixteen hours at 145°. Two 10-cc. portions of pure anhydrous ether were used to separate the unchanged ester from the phthalic anhydride.

Mono-ethyl Phthalate.—Twenty-five grams of phthalic anhydride was dissolved in 200 cc. of absolute ethyl alcohol (calcd. amt. × 20.4) by refluxing the mixture for two hours on a water-bath. Removal of the alcohol by distillation produced a sirupy liquid. In order to separate the mono-ethyl ester from diethyl phthalate, the product was dissolved in 100 cc. of water. The solution was maintained at its boiling point for an hour, and 25 g. of powdered barium carbonate was added during this period. The neutral mixture was cooled to room temperature and filtered; the filtrate was acidified with concd. hydrochloric acid and extracted with 100 cc. of ether. After the ether solution had been shaken with 10 cc. of water, it was dried overnight with 5 g. of an-

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[4] Underwood and Clough, THIS JOURNAL, 51, 583 (1929).

hydrous sodium sulfate and then filtered. The ether was removed by distillation on a water-bath. After drying in a vacuum desiccator over anhydrous calcium chloride, the product weighed 8 g. (24.4% yield).

By use of the procedure described above, we obtained 7.5 g. of phthalic anhydride (98.4% yield) by heating 10 g. of mono-ethyl phthalate with 20 g. of glacial acetic acid and 30 g. of acetic anhydride at 145° for sixteen hours. Two cc. of impure ethyl acetate was secured by several fractionations of the distillate. Ten grams of mono-ethyl phthalate yielded 4.7 g. of phthalic anhydride when heated at 145° for sixteen hours.

The results of our experiments show that the hydroxyl and alkoxyl groups in mono-methyl and mono-ethyl phthalates are loosely held.

Dimethyl and Diethyl Phthalates.—Ten g. of each of these compounds was heated with 20 g. of glacial acetic acid and 30 g. of acetic anhydride for sixteen hours at 145°, and the mixture was then fractionated. In each case, practically all of the ester was recovered unchanged.

Phthalamic Acid.—Acidification of a solution of 50 g. of phthalimide in 150 g. of 25% potassium hydroxide solution (calcd. amt. × 1.97) with concd. hydrochloric acid, gave a light brown precipitate. This was collected on a filter, ground with three 25-cc. portions of water in a mortar and dried. The yield of phthalamic acid, m. p. 147–148°, was 43.2 g. (77%).

After a mixture of 10 g. of phthalamic acid (the mono-amide of phthalic acid), 20 g. of glacial acetic acid and 30 g. of acetic anhydride had been refluxed for sixteen hours at 145°, practically all of the liquid was removed by distillation and the residue was stirred with 100 cc. of alcohol. The insoluble material was collected on a filter, washed and dried; this substance, which weighed 4.2 g., was identified as phthalimide. Evaporation of the filtrate to dryness gave 4.73 g. of phthalic anhydride. Ten grams of phthalamic acid was converted into 6.0 g. of phthalimide and 2.9 g. of phthalic anhydride by heating at 145° for sixteen hours. The products were separated by treatment with alcohol.

In "Beilstein" it is stated that phthalamic acid decomposes smoothly at 155° into phthalimide and water, and that treatment with glacial acetic acid transforms phthalamic acid into phthalic anhydride.

Phthalamide.—A mixture of 25 g. of phthalimide and 100 cc. of concd. ammonium hydroxide (*d* 0 9; calcd. amt. × 9.03) was maintained at its boiling point for twenty minutes, and then allowed to cool to room temperature. The precipitated phthalamide was collected on a filter, washed with 20 cc. of 5% ammonia solution and dried for half an hour at 100°. The product weighed 25.8 g. (92.5% yield) and melted at 219–220° with evolution of ammonia.

The solution obtained upon heating 10 g. of phthalamide, 20 g. of glacial acetic acid and 30 g. of acetic anhydride at 145° for an hour was cooled in ice. The precipitate which formed was collected on a filter and dried; it weighed 4.5 g. and melted at 170–172°. The properties of this substance indicated that it was o-cyanobenzamide. Practically all of the liquid in the filtrate was removed by distillation at 145'. When the residue was cooled in ice, it deposited a colorless solid which weighed 3.7 g. after drying. This product was identified as phthalimide. Ten g. of phthalimide was unchanged by heating for an hour at 145".

In Beilstein it is stated that treatment with acetic anhydride (free from acetic acid) converts phthalamide into o-cyanobenzamide, phthalonitrile, phthalimide and acetylphthaliide.

Summary

Fusion with potassium hydroxide converts phenoldiphenein into the potassium salts of phenol and o-pbenylbenzoic acid. The lactone di-

methyl ether of phenoldiphenein is formed by treatment of the latter with methyl iodide and potassium hydroxide and by the reaction of diphenic anhydride with anisole in the presence of anhydrous aluminum chloride. The presence of two acidic hydrogen atoms in phenoldiphenein is shown by analysis of the potassium salt. These transformations indicate that the structure of phenoldiphenein is similar to that of phenolphthalein and that the sodium salt of phenoldiphenein contains a quinoid ring. The groups in this salt give it a light yellow instead of a red color.

When dimethyl phthalate and diethyl phthalate are heated with acetic anhydride, each ester remains unchanged. Under similar conditions the monomethyl and mono-ethyl esters of phthalic acid yield phthalic anhydride. Phthalamic acid is converted into phthalimide and phthalic anhydride by treatment with acetic anhydride, and phthalamide gives *o*-cyanobenzamide and phthalimide.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION NO. 62 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

PREPARATION OF SOLID DERIVATIVES FOR THE IDENTIFICATION OF ETHERS

BY H. W. UNDERWOOD, JR., O. L. BARIL AND G. C. TOONE[1]

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Ethers are usually described as inert compounds; the carbon–oxygen bond is firmly held, and drastic treatments, such as heating with hydriodic acid or anhydrous aluminum chloride, are generally employed to split ethers. These methods are not suitable for the preparation of solid derivatives for the identification of small amounts of ethers. Recently it was shown that ethyl 3,5-dinitrobenzoate is formed by the treatment of the dinitrobenzoyl chloride with pure, dry ethyl ether in the presence of anhydrous zinc chloride.[2] This paper describes the preparation of crystalline 3,5-dinitrobenzoates from small amounts of representative, simple aliphatic ethers. Procedures for the conversion of typical aromatic ethers into crystalline bromo derivatives are also discussed.

Discussion of Experiments

All the temperatures given are uncorrected.

Purification of Ethers.—The aliphatic ethers were purified by the method described in a previous paper.[3] Experiments with samples of

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[1] Some of the experimental results described in this and a previous paper are taken from a thesis submitted to the Faculty of the Massachusetts Institute of Technology by G. C. Toone in partial fulfilment of the requirements for the degree of Master of Science. The bromo derivatives of the aromatic ethers were prepared by O. L. Baril.

[2] Underwood and Wakeman, THIS JOURNAL, 52,387 (1930).

[3] Underwood and Toone, *ibid.*, 52, 391 (1930).

all the aliphatic ethers, except isobutyl and n-hexyl, obtained from the Eastman Kodak Company gave results similar to those obtained with the purified compounds.

Reactions of Simple Aliphatic Ethers with 3,5-Dinitrobenzoyl Chloride

General Procedure.—One cubic centimeter of each ether was added to a mixture of 0.1–0.15 g. of finely powdered, anhydrous zinc chloride and 0.5 g. of 3,5-dinitrobenzoyl chloride in a dry 7.6-cm. test-tube. A small reflux water condenser, constructed from two pieces of glass tubing, was attached immediately, and the mixture was refluxed gently by heating in an oil-bath for about one hour. The product was then poured into a small beaker. The test-tube was rinsed with 10 cc. of 1.5 N sodium carbonate solution and this was added to the reaction mixture. The contents of the beaker were stirred and heated in a water-bath, maintained at 90–100°, for about one minute. The mixture was allowed to stand at room temperature for five minutes, and then filtered by suction. The precipitate was washed on the filter with 5 cc. of 1.5 N sodium carbonate solution and with two 5-cc. portions of water, and then drained thoroughly. The solid was transferred to a 15-cm. test-tube and extracted with 10 cc. of carbon tetrachloride, kept at its boiling point by heating over a free flame, for about three minutes. The hot mixture was filtered immediately and the filtrate was evaporated to dryness by a current of air. The residue was crystallized from 2–3 cc. of carbon tetrachloride. Crystallization was facilitated by cooling the solution in ice. The crystals were dried in the air. The yield of alkyl 3,5-dinitrobenzoate was 0.1–0.15 g.

The ethers investigated and the melting points of the 3,5-dinitrobenzoates obtained are as follows: ethyl, 92–93°; n-propyl, 73.5–74°; isopropyl, 120–121°; n-butyl, 62–63°; isobutyl, 84.5–85.5°; n-amyl, 42–43°; iso-amyl, 60–61°; n-hexyl, 54.5–55.5°. In some experiments it was necessary to evaporate the carbon tetrachloride solutions of the products from n-amyl, iso-amyl and n-hexyl ethers almost to dryness in order to isolate the esters, and subsequently to recrystallize the latter from about 2 cc. of ethyl alcohol. Carbon tetrachloride was used instead of alcohol in our experiments in order to avoid reactions of unchanged dinitrobenzoyl chloride with the alcohol.

Several investigators have given different melting points for alkyl dinitrobenzoates.[4] Each melting point, except that of the n-amyl ester which is listed as 44.4–44.6° by Tseng,[4] obtained by us agrees with one previously reported. We found that we could raise the melting point of n-amyl

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[4] Malone and Reid, THIS JOURNAL, 51, 3426 (1929); Reichstein, Helv. *Chim. Acta*, 9, 802 (1926); Majima, Nagaoka and Yamada, Ber., 55, 215 (1922); Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, 1904, Vol. I, pp. 168–172; Research on derivatives of alcohols carried out at the Massachusetts Institute of Technology by Tseng under the direction of Professor Mulliken.

3,5-dinitrobenzoate by preparing a relatively large amount of the ester and recrystallizing it several times from ethyl alcohol. The melting points given above are those usually obtained under the conditions we used. We checked the identity of our products by mixed melting points with samples of alkyl dinitrobenzoates prepared from pure alcohols.

Reactions of Aromatic Ethers

Anisole, Phenetole and *p*-Nitrobenzoyl Chloride.—It has been noted that diphenyl ether and anisole behave like aromatic hydrocarbons when heated with acetyl and benzoyl chlorides in the presence of anhydrous zinc chloride; ketones are formed by the introduction of an acetyl or benzoyl group into the aromatic nucleus.[2] The reactions of these (and other aromatic) ethers with 3,5-dinitrobenzoyl chloride gave products which had undesirable properties.

4'-Nitro-4-methoxybenzophenone and 4'-nitro-4-ethoxybenzophenone were readily prepared from anisole and phenetole. A mixture of 1 cc. of each ether, 0.8 g. of pure *p*-nitrobenzoyl chloride, 1 cc. of dry carbon disulfide and 0.1 g. of granular, anhydrous aluminum chloride was placed in a dry 7.6-cm. test-tube, and warmed gently over a free flame to start the reaction. After the evolution of hydrogen chloride had subsided, a small water condenser, constructed from two pieces of glass tubing, was attached to the tube and the mixture was refluxed gently for half an hour by heating in an oil-bath. The contents of the tube were rinsed into a small beaker with 15 cc. of water and allowed to cool. The mixture was next extracted, in a separatory funnel, with a 15-cc. and a 5-cc. portion of ether. The combined ether layers were shaken with 15 cc. of 10% sodium hydroxide solution, and then dried with 1 g. of anhydrous sodium sulfate for half an hour. The dry ether solution was decanted and the solvent was allowed to evaporate under a hood. The solid residue was crystallized two or three times from 5 cc. of alcohol. Our 4'-nitro-4-methoxybenzophenone melted at 120.5–121°, and the 4'-nitro4-ethoxybenzophenone melted at 110.5–111°. These compounds are listed in Beilstein; the melting point of the ethoxy derivative is given as 112". We found no references to the preparation of these substances from small amounts of the ethers. It is believed that our products are the most satisfactory solid derivatives now available for anisole and phenetole.

Attempts to prepare *p*-nitrobenzoyl derivatives of naphthyl, benzyl and other aromatic ethers gave oils which would not crystallize. Consequently, it was decided to investigate another reaction for ethers containing aromatic groups.

Bromination of Aromatic Ethers.—Procedures for the preparation of crystalline bromo derivatives from representative aromatic ethers were devised; details are given in Table I.

The bromo derivatives of *o*-cresylmethyl, benzyl, α-naphthylmethyl and β-naphthylmethyl ethers are new compounds. The other products are listed in Beilstein, but we found no references to the preparation of these compounds from small amounts of the ethers. In most cases it was necessary to modify considerably the preparative methods given in the literature; the rate of addition of bromine and temperature control are particularly important.

Brominations of anisole and phenetole gave oils which would not solidify.

Anal. Monobromo-*o*-cresyl methyl ether. Calcd. for C_8H_9OBr: Br, 39.76. Found: Br, 39.38, 39.41. Dibromobenzyl ether. Calcd. for $C_{14}H_{12}OBr_2$: Br, 44.90. Found: Br, 44.76, 44.79. Monobromo-a-naphthyl methyl ether. Calcd. for $C_{11}H_9OBr$: Br, 33.73. Found: Br, 33.69, 33.65. Monobromo-β-naphthyl methyl ether. Calcd. for $C_{11}H_9OBr$: Br. 33.73. Found: 33.68, 33.67.

Table I

Experimental Results

No.	Ether			Bromine			Solid formed in
		G.	Solvent	G.	Solvent	Added in minutes	
1	*o*-Cresyl methyl	0.31	2 cc. alc.	0.42	....	5, drop by drop	10 minutes
2	Guaiacol	.31	3 cc. alc.	1.5	3 cc. alc.	8. Note *a*	Note *a*
3	Veratrole	.35	5 cc. alc.	0.84	3 cc. alc.	5	Note *b*
4	Resorcinol dimethyl	.35	3 cc. alc.	.88	....	5	At once
5	Hydroquinone dimethyl	.35	1 cc. gl. HAc	.84	1 cc. gl. HAc	5	At once
6	Anethole	.37	4 cc. abs. ether	.84	3 cc. abs. ether	8, drop by drop[e]	Note *e*
7	Safrole	.41	3 cc. alc.	2.0	....	8. Note *f*	At once[f]
8	Isosafrole	.41	2 cc. CS_2	2.03	....	15, drop by drop	24 hours
9	Eugenol methyl	.45	5 cc. dry ether	.8	....	10. Note *h*	Note *h*
10	Isoeugenol methyl	.45	5 cc. dry ether	.4	....	8. Note *h*	Note *h*
11	Diphenyl	.43	2 cc. alc.	.8	....	10, drop by drop	Overnight
12	Benzyl	.5	1 cc. alc.	.8	....	5	Overnight
13	α-Naphthyl methyl	.4	3 cc. $CHCl_3$	.42	....	8, drop by drop[i]	Overnight
14	β-Naphthyl methyl	.4	2 cc. gl. HAc	.42	....	3	5 minutes
15	α-Naphthyl ethyl	.43	3 cc. $CHCl_3$	.42	....	5	Overnight[j]
16	β-Naphthyl ethyl	.43	1 cc. gl. HAc	.42	....	3. Note *k*	10 minutes

TABLE I (*Concluded*)

No.	Products				
	Derivative	Crystallized from	Form	G.	M. p., °C.
1	Monobromo	8 cc. alc.	Plates	0.46	63–64
2	Tribromo	3 cc. alc.	Needles	.7	115.5–116
3	Dibromo	2 cc. alc.	Prisms	.25	92–92.9
4	Dibromo	8 cc. alc., twice[c]	Needles	.55	140–141
5	Dibromo	15 cc. gl. HAc[d]	Needles	.69	142
6	Monobromo dibromide	18 cc. pet. ether[e]	Needles	.68	107.6–108
7	Tribromo dibromide	7 cc. benzene	Needles	1.14	169–170
8	Monobromo dibromide	5 cc. pet. ether[g]	Needles	0.55	109
9	Monobromo dibromide	8 cc. abs. alc. at 60°[h]	Needles	.88	77.5–78
10	Dibromide	8 cc. dry ether	Plates	.61	101–101.5
11	Dibromo	6 cc. alc.	Leaflets	.94	54–55
12	Dibromo	10 cc. alc.	Plates	.47	107–108
13	Monobromo	8 cc. alc.	Needles	.6	46
14	Monobromo	18 cc. pet. ether	Plates	.63	62–63
15	4-Bromo	10 cc. alc.	Prisms	.55	47.8
16	1-Bromo	15 cc. pet. ether	Plates	.48	66.1

[a] The mixture of guaiacol and bromine was heated for twenty minutes on a water-bath. After the alcohol had been removed by distillation, 1 cc. of glacial acetic acid was added; crystallization occurred at once. [b] The reaction mixture obtained from veratrole was diluted with 40 cc. of water, stirred, allowed to stand for two hours and filtered. [c] Before crystallization, dibromoresorcinol dimethyl ether was washed with 1 cc. of alcohol. [d] The dibromo derivative of hydroquinone dimethyl ether was washed with 3 cc. of 80% acetic acid before crystallization. [e] The ether solution of anethole was cooled in ice during the addition of bromine; the crystals formed when the solvent evaporated were ground with 1 cc. of cold alcohol in a mortar before crystallization. [f] The mixture of safrole and bromine was heated for fifteen minutes on a water-bath. [g] Before crystallization, the impure monobromo-isosafrole dibromide was ground in a mortar with 3 cc. of cold alcohol. [h] During the addition of bromine the ether solutions of eugenol methyl ether and of isoeugenol methyl ether were cooled in ice. Subsequently the reaction mixtures were allowed to stand for half an hour at room temperature, and then cooled in a bath of ice and concd. hydrochloric acid. Crystallization was induced by scratching the wall of the container with a sharp glass rod. Monobromo-eugenol methyl ether dibromide was washed with 3 cc. of cold alcohol before crystallization. [i] The chloroform solution of α-naphthyl methyl ether was cooled in ice during the addition of bromine and for fifteen minutes longer; subsequently it was allowed to stand overnight at room temperature. [j] In some experiments with α-naphthyl ethyl ether the bromo derivative crystallized only when allowed to stand for a long time. [k] The reaction mixture obtained from β-naphthyl ethyl ether was cooled for ten minutes after the addition of bromine.

Oxidation of Cresyl Ethers.—Brominations of p-cresyl methyl, *p*-cresyl ethyl and o-cresyl ethyl ethers gave oils which would not solidify. Details of a procedure for the oxidation of these compounds to anisic, *p*-ethoxybenzoic and o-ethoxybenzoic acids are given below. A mixture of 0.5 g. of the ether, 2.5 g. of concd. sulfuric acid, 37 cc. of water and 1.75 g. of powdered potassium dichromate was heated at its boiling point in a flask connected with a reflux water condenser. The periods of heating were four, three and two hours, respectively. The mixture was cooled to room temperature, diluted with 50 cc. of water, transferred to a separatory funnel and extracted with 30. 10 and 10-cc. portions of ether. The combined ether layers were shaken with 25 cc. of 10% sodium carbonate solution. The sodium carbonate extract was acidified with 20 cc. of 6 *N* hydrochloric acid. The precipitated anisic and *p*-ethoxybenzoic acids were collected on a filter, washed with 5 cc. of water and crystallized from 50 cc. of hot water and from 10 cc. of alcohol, respectively. o-Ethoxybenzoic acid was precipitated as an oil; this was extracted with two 25-cc. portions of ether. The ether solution was dried with 2 g. of anhydrous sodium sulfate for an hour, decanted and allowed to stand until the solvent evaporated. About 0.1 g. of an oil which melted at 19–19.5' was thus obtained. The yields of anisic and *p*-ethoxybenzoic acids were 0.2 and 0.3 g.; the products melted at 183.9 and 195.2–195.5°, respectively.

Summary

Small amounts of ethyl, n-propyl, isopropyl, n-butyl, isobutyl, *n*-amyl, iso-amyl and n-hexyl ethers are converted into the corresponding 3,5-dinitrobenzoates by treatment with 3,5-dinitrobenzoyl chloride in the presence of anhydrous zinc chloride. The reactions of *p*-nitrobenzoyl chloride with small quantities of anisole and phenetole give 4'-nitro-4-methoxybenzophenone and 4'-nitro-4-ethoxybenzophenone. Crystalline bromo derivatives can be readily prepared from small amounts of o-cresyl methyl, resorcinol dimethyl, hydroquinone dimethyl, eugenol methyl, isoeugenol methyl, diphenyl, benzyl, a-naphthyl methyl, *β*-naphthyl methyl, *α*-naphthyl ethyl and *β*-naphthyl ethyl ethers, guaiacol, veratrole, anethole, safrole and isosafrole. The oxidation of *p*-cresyl methyl, P-cresyl ethyl and o-cresyl ethyl ethers on a small scale gives anisic, *p*-ethoxybenzoic and o-ethoxybenzoic acids.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY NO. 636]

THE ACTION OF ULTRAVIOLET LIGHT ON TERPENES. I. THE ACTION ON CITRONELLAL

BY MARSTON TAYLOR BOGERT AND TORSTEN HASSELSTRÖM[1]

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As is well known,[2] citronellal can be changed into isopulegol or its derivatives by the action of acids or acid anhydrides. In fact, isopulegol is most conveniently prepared in the laboratory by the action of acetic anhydride upon citronellal, and the mechanism of this reaction has been elucidated by Semmler,[2f] who found that the aldehyde was changed first into its enol acetate, which then added a second molecule of acetic acid with formation of a diacetate, this diacetate in turn splitting out a mole of acetic acid again in such manner that ring closure was effected and isopulegol acetate produced.

When such acids as formic or phosphoric are used as condensing agents, hydrates of isopulegol are obtained, as shown by Prins.[2h]

Labbe[3] observed that citronellal on standing gradually changed almost wholly to the isomeric isopulegol. A sample which nearly completely filled its container, after standing for two months, no longer exhaled any citronellal odor or gave any appreciable reaction with bisulfite, but when oxidized with dichromate and sulfuric acid yielded isopulegone.

Sernagiotto[4] likewise noted that when citronellal was exposed to direct sunlight, in the presence of air and moisture, isopulegol was formed, as well as dihydroxycitronellic acid. The conditions under which this experiment and that of Labbe[3] were carried out, however, were such as to make it desirable to ascertain the effect of ultraviolet light alone upon the aldehyde.

For this purpose, citronellal was placed in a closed quartz vessel and exposed to ultraviolet light, the effect of this exposure being followed by noting the gradual rise in the refractive index. Examination of the product showed that a considerable amount of the citronellal had been changed into isopulegol. This conversion must have been due therefore chiefly to the action of the light rays and not to an hydration–dehydration reaction, since all moisture had been excluded.

To prove that under these conditions also the enol form of citronellal

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[1] Rockefeller Foundation Fellow, 1929–1930.

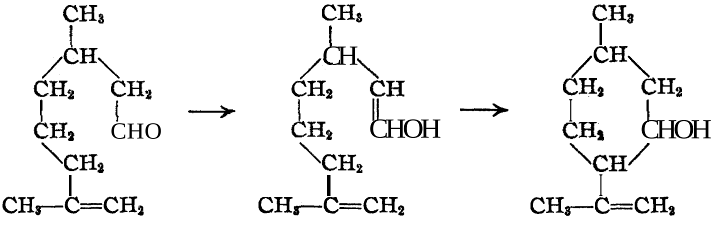
[2] (a) Dodge, THIS JOURNAL, 11, 464 (1889); (b) Dodge, *ibid.*, 12, 555 (1890); (c) Tiemann and Schmidt, *Ber.*, 29, 913 (1896); (d) Barbier and Leser, *Compt. rend.*, 124, 1308 (1897); (e) Wegscheider and Späth, *Monatsh.*, 30, 825 (1909); (f) Semmler, *Ber.*, 42, 2015 (1909); (g) Dodge, THIS JOURNAL, 37, 2756 (1915); (h) Prins. *Chem. Weekblad*, 14, 627 (1917).

[3] Labbe, *Bull. soc. chim.*, [3] 21, 1023 (1899).

[4] Sernagiotto, *Atti accad. Lincei*, [5] 24 850 (1915).

was probably the intermediate product, some of this enol acetate was prepared by the method of Semmler[2f] and exposed to the ultraviolet rays. Isopulegol acetate was formed.

It is believed therefore that the effect of the ultraviolet rays upon citronellal (I) is to rearrange it first to the enol formation (II), and then to close the latter to the cyclic isopulegol (III)



I II III

This hypothesis is supported further by the facts that reagents effective in accomplishing this ring closure have been shown to function as enolizing agents, and because the enol being the unstable form of the aldehyde it has been observed by Stoermer[5] that light can change the stable forms of certain compounds into unstable tautomers.

Several investigators[6] have observed that the action of light upon aldehydes often results in the production also of di- and trimolecular polymers. It is worth noting, therefore, that in our own experiments a trimolecular polymer of citronellal was isolated among the products formed by the action of the ultraviolet light. Prins[2h] reported a dimolecular polymer as one of the products when formic acid acted upon citronellal.

That "citronellal," as ordinarily obtained, is probably an equilibrium mixture of two structural isomers, one, the so-called "alpha" or "limonene" **form,** corresponding to Formula (I) above, and the other, the "beta," "terpinolene" or "rhodinal" form, $(CH_3)_2C{=}CH(CH_2)_2CH(CH_3)CH_2$-CHO, seems indicated by the reports of various workers.[2h,7]

The nature of the citronellal used in our experiments is described beyond. Although both forms yield isopulegol when treated with strong

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[5] (a) Stoermer and Simon, *Ann.*, **342**, 11 (1905); (b) Stoermer, *Ber.*, 42, 4867 (1909).

[6] (a) Benrath, *J. prakt. Chem.*, [2] 72, 220 (1905); (b) Ciamician and Silber, *Ber.*, 44, 1558 (1911); (c) Benrath, *J. prakt. Chem.*, [2] 86, 336 (1912); (d) Franke and Pollitzer, *Sitz. Akad. Wiss. Wien*, Abt. IIb, 122, 183 (1913); *Monatsh.*, 34, 797 (1913); (e) Stobbe and Lippold, *J. prakt. Chem.*, [2] 90, 277, 280 (1914).

[7] (a) Semmler, *Ber.*, 26, 2257 (1893); (b) Barbier and Bouveault, *Compt. rend.*, 122, 737 (1896); *(c)* Tiemann and Schmidt, *Ber.*, **30**, 33 (1897); (d) Harries and Roeder, *ibid.*, 32, 3357 (1899); (e) Bouveault, *Bull. soc. chim.*, [3] 23, 458, 463 (1900); (f) Harries and Schauwecker, *Ber.* 34, 1498, 2981 (1901); (g) Harries and Himmelmann, ibid., 41, 2187 (1908); (h) Harries, *Schimmel's Ber.*, October, 1915, p 78; (i) Grignard and Doeuvre, *Compt. rend.*, 187, 270 (1928); (j) Grignard and Doeuvre, *ibid.*, 187, 330 (1928); (k) Verley, *Bull. soc. chim.*, [3] *43*, *845* (1928); (l) Doeuvre, *ibid.*, [3] 47, 323 (1930).

acids, it is our belief that, under the action of ultraviolet light, the alpha tends to produce isopulegol mainly and the beta the polymer

$$\begin{tikzcd}
\text{a-Form} \arrow[r] \arrow[d, shift left] & \text{isopulegol} \arrow[d] \\
\beta\text{-Form} \arrow[r] \arrow[u, shift left] & \text{polymer}
\end{tikzcd}$$

If, then, light alone is capable of changing citronellal into isopulegol and higher polymers, it is of considerable significance for phytochemistry and botany as a plausible, or at least possible, explanation of the origin of certain cyclic terpenes found in the vegetable kingdom.

Experimental Part

Apparatus.—The source of the ultraviolet light was a mercury vapor lamp manufactured by the Hanovia Chemical and Manufacturing Company, of Newark, N. J., and known as the "Advanced Research Lamp," with an average life of about **4000** hours. The container for the material to be exposed to the rays was a quartz box, 10 X 5 X 1 cm., furnished with quartz inlet and outlet tubes, which were kept closed with rubber tubing during the experiments. This box was placed four inches from the burner and its temperature was maintained at **45–50'** by a stream of air. In Runs A and B, Table I, the box was filled completely by the citronellal. In Run C, the quantity of aldehyde available was not enough for this, so the space remaining was filled with dry carbon dioxide, to prevent oxidation, and this was done also in Run B after the removal of the sample for analysis following fifty hours' exposure.

Citronellal.—A high-class commercial article, supplied through the courtesy of Fritzsche Brothers, of New York, was used as initial material; b. p. **200–202°**, d^{m} **0.8578**, n_{D}^{22} **1.44991**, α_{D}^{30} +4°22′ (2 = 0.5 dm.).

To determine the amount of non-volatile impurities present, 5 g. of the aldehyde was distilled with steam. What remained in the distilling flask was extracted repeatedly with ether, the ether extracts dried and the ether driven off. There remained **0.02** g. of a yellow oil, equivalent to 0.4% of the original aldehyde.

The determination of the non-aldehydic content of the volatile material was based upon the experiments of Tiemann and Schmidt[7c] which proved that citronellal condenses quantitatively with semicarbazide under proper conditions. Three grams of the steam-distilled aldehyde, which had been dried with anhydrous sodium sulfate, was poured into an aqueous solution of 3 g. of semicarbazide hydrochloride and 3 g. of anhydrous sodium acetate. Alcohol was added to this solution until it became slightly opalescent. The mixture was kept at room temperature overnight, then heated for six hours at 60–70°, after which it was transferred to a larger flask and distilled with steam. The oil driven over by the steam was collected with ether, the ether extracts dried with anhydrous sodium sulfate and the ether removed. There remained **0.25** g. of oil, or 8.3% of the original aldehyde.

In conducting the runs recorded in Table I, the change in refractive index of the citronellal was determined with a Pulfrich refractometer at the intervals indicated. It will be noted that indices recorded in Runs B and C are mostly lower than in Run A, for the same total exposure, and this we believe can be ascribed, in part at least, to the decreasing activity of the lamp with use.

After exposure, as shown in Table I, samples were removed and analyzed for non-volatile and for volatile non-aldehydic content by the methods given above. The refractive index for the volatile non-aldehydic material obtained was also recorded. These data are given in Table II.

Examination of the volatile non-aldehydic material separated (from Run A after

177.5 hours' exposure, which amounted to **27.9%.—It** was distilled under reduced pressure. Practically all came over at **90–91°** at **9 mm.** pressure and showed the properties of isopulegol, including d^{20} **0.9125** and n_D^{22} **1.47078,** as compared with $d^{17.5}$ **0.9154** and n_D^{20} **1.47292** as recorded for isopulegol in the literature.''

This product (**3.2** g.) was oxidized to isopulegone by potassium dichromate and sulfuric acid, as described by Tiemann and Schmidt,[7c,8] except that sodium bicarbonate was added to the oxidized mixture before it was distilled with steam. The ketone recovered (**2** g.) was converted into its semicarbazone which, after two recrystallizations from dilute alcohol, formed colorless needles, m. p. 183° (uncorr.), in agreement **with** the figure **given** in the literature[9] for the inactive isopulegone semicarbazone.

Anal. Calcd. for $C_{11}H_{19}ON_3$: N, **20.10.** Found: N, **19.95.**

Tiemann and Schmidt obtained the active semicarbazone by their process.

Examination of that Portion of **the** Exposed Aldehyde which was not Volatile **with** Steam.—This portion was recovered, by the method already described, by ether extraction of the mixture remaining in the distilling flask after subjecting to steam distillation that sample of exposed citronellal (Run **A)** used above **for** the determination of volatile non-aldehydic constituents. The viscous yellow oil **(62.1%)** left after the evaporation of the dried ether could not be distilled without decomposition. After being kept in an evacuated desiccator for several weeks, to remove all traces of ether or moisture, it was analyzed and its molecular weight determined.

Anal. Calcd. for $(C_{10}H_{18}O)_x$: C, **77.92;** H, **11.69.** Found: *C,* **78.23;** H, **11.50.** Mol. wt. found. **466.7** and **460.8; calcd.** for $C_{30}H_{54}O_3$, **462.4.**

These results lead to the conclusion that the product was a **trimolecular** polymer of citronellal.

Examination of the curve plotted from Run A discloses some irregularity and flattening in the middle region, and it was to learn more about this that Run B was carried out and the content of volatile non-aldehydic and of non-volatile material determined after 50 and after 118 hours' exposure (see Table II). These results indicate a condition approaching

TABLE I

EXPERIMENTAL RESULTS

Citronellal,[10] n_D^{20} 1.4461 Isopulegol,[7c] n_D^{20} 1.47292

Run A Total hours exposed	n_D^{22}	Run A Total hours exposed		Run B Total hours exposed	n_D^{22}	Run C Total hours exposed	n_D^{22}
0	1.44991	88	1.46566	6.5	1.45031	20	1.45271
8.5	1.44981	99	1.46763	16.5	1.45151	40	1.45441
18	1.45091	109	1.46862	26	1.45281		
21.5	1.45101	120	1.47009	33	1.45371		
28	1.45291	129.5	1.47107	50	1.45561		
38	1.45571	139	1.47205	63	1.45711		
48	1.45761	148.5	1.47312	75	.1.45811		
55	1.46199	160.5	1.47362	87	1.45921		
62	1.46347	167.5	1.47470	100	1.46283		
76	1.46497	177.5	1.47523	118	1.46318		

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[8] Tiemann and Schmidt, *Ber.*, **32, 3257 (1899).**

[9] (a) Harries and Roeder, *ibid.*, **32,3371 (1899);** (b) Wallach, **Ann., 365,252 (1909).**

[10] Tiemann, *Ber.*, **32,818** (1899).

TABLE II

RESULTS OF EXPERIMENTS

Run	Total hours of exposure	Nan-volatile, %	Volatile non-aldehydic %	Volatile non-aldehydic n_D^{22}
	0	0.4	8.3	1.46387
C	20	12	18.7	1.46852
C	40	20	28.1	1.47051
B	50	34.4	32.1	1.46783
B	118	34.4	34.4	1.46931 (n_D^{26})
A	177.5	62.1	27.9	1.47078

The refractive index of the volatile non-aldehydic portion was determined on the distilled oil in Run A, but on the undistilled material from Runs B and C.

equilibrium in this region. The variation in the refractive index during this period of temporary equilibrium may be due to a change in the character of this non-volatile material, rather than in its total amount, after which change the curve resumes its normal course. Similarly, the fall in volatile non-aldehydic ingredients after 118 hours' exposure is believed to be due to polymerization of the isopulegol.

The Action of Ultraviolet Light upon the Enol Acetate of Citronellal.—This was prepared by the method of Semmler[2f] and showed the following constants: b. p. (10 mm.) 110–115°, d^{20} 0.9068, n_D^{28} 1.44801.

Fifteen grams of this acetate was placed in the quartz box, the remaining space in the box being filled with dry carbon dioxide, and was exposed to the ultraviolet light, the changes produced in the enol acetate being followed by determining the changes in its density. The results are presented in Table III.

TABLE III

EXPERIMENTAL DATA

Total hours exposed	d^{20}
0	0.9068
7	.9078
16	.9102
26	.9122
38	.9236
46	.9238

Citronellal enol acetate,[2f] d^{20} 0.902, n_D 1.45762. Isopulegol acetate,'' d^{20} 0.925, n_D 1.459

Upon the conclusion of this exposure, 14 g. of the exposed enol acetate was repeatedly distilled under diminished pressure. On the sixth distillation, the following fractions were collected.

Fraction	B. p. at 10 mm., °C.	Amt., g.	d^{20}	n_D^{26}
1	90–105	1.5	0.9168	1.45541
2	105–107	7	.9278	1.45691
3	107–125	3	.9054	1.45341

There remained in the distilling flask only a small quantity of viscous oil.

Fraction 1 was not examined, but its high density would indicate that it was composed chiefly of isopulegol acetate.

Fraction 2 was analyzed with the following results.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.47; H, 10.20. Found: C, 73.0; H, 10.14.

These analytical figures, taken together with the density and refractive index of this fraction, supported the conclusion that it was mainly isopulegol acetate. It (4 g.) was therefore saponified by an alcoholic potassium hydroxide solution and the mixture distilled with steam. The volatile oil was extracted from the distillate with ether, the ether evaporated and the residual isopulegol oxidized by dichromate and sulfuric acid to the isopulegone, whose semicarbazone was prepared and melted at 183° (uncorr.). This product, when mixed with the inactive isopulegone semicarbazone obtained from citronellal itself, as already reported, showed no change in melting point.

Fraction 3 contained unchanged enol acetate.

Summary

1. Citronellal can be changed to isopulegol by the action of ultraviolet light, a fact which is of considerable significance to phytochemistry as well as to botany.

2. The mechanism of the reaction is believed to consist first in the rearrangement of the aldehyde into its enol formation, which then closes to the cyclic isopulegol, since it is shown that citronellal enol acetate also can be converted into isopulegol acetate by ultraviolet light.

NEW YORK, N. Y.

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

STEREOCHEMISTRY OF DIPHENYLBENZENES. PREPARATION OF STEREOISOMERIC 3,6-DI-(2,4-DIMETHYLPHENYL)-2,5-DIBROMOHYDROQUINONES AND THEIR DERIVATIVES. IX[1]

BY E. BROWNING[2] AND ROGER ADAMS

RECEIVED JULY 25, 1930 PUBLISHED OCTOBER 6, 1930

In a recent article[3] on the isomerism of diphenyl compounds it was pointed out that interesting possibilities for stereoisomerism existed in diphenylbenzene derivatives if the same conditions were found in these latter molecules that produced isomerism in diphenyl derivatives. Thus. for example, in a molecule of type (I) in which each of the two end benzene rings are asymmetric in themselves and similar to each other, meso and racemic modifications should exist. The meso form is of peculiar interest

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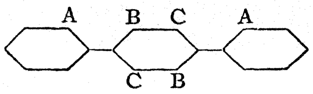
[1] For article No. VIII in this series see Stanley and Adams, THIS JOURNAL, 52, November, 1930.

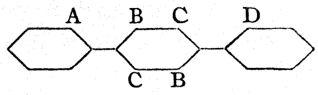
[2] This communication is the abstract of a thesis submitted by E. Browning in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Stanley and Adams. *Rec. trav. chim.*, 48,1035 (1929).

in that it contains a point of symmetry in distinction to a plane of symmetry found usually. If, on the other hand, the two end rings are dissimilar to each other (II), but still asymmetric in themselves, two racemic modifications should be possible. A third even more interesting type is that found in a formula of type (III) in which optical isomerism is not possible of existence but *cis–trans* isomers should occur whether the two end rings are similar or dissimilar, provided each is asymmetric in itself.



I



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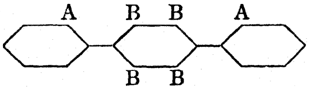

III

Investigations on these compounds are now under way in this Laboratory and the preliminary results are being presented in this communication on the study of compounds of type (I). In a recent article, Kogl and Erxleben,[4] who, apparently, had not read the communication from this Laboratory which contained a discussion of diphenylbenzene isomerism and a statement of the intention to undertake here a study of this problem experimentally, announced that they are planning to work on the resolution of terphenyl derivatives. The authors of this article, as they have established priority, desire to reserve this field for the next few years or until such a time, at least, as the predictions set forth by them in the article mentioned may be verified or disproved.

The specific compound which has been selected for study in this initial investigation is a derivative of 3,6-di-(2,4-dimethylphenyl)-hydroquinone (IV). This latter substance can, fortunately, be obtained with readiness following the general procedure of Pummerer.[5] A 50% yield of product was obtained by condensation of *m*-xylene with *p*-benzoquinone. This substance in itself has only two ortho substituents in each set of four positions existing adjacent to the linkages between the benzene rings. Past experience has shown that at least three groups are necessary in the adjacent positions before free rotation between the benzene rings is prevented. The compound, however, lends itself well to the satisfying of such conditions by the formation of a derivative which has these properties. Upon bromination with two moles of bromine in chloroform as a solvent, there is obtained a reaction mixture which, after reduction to remove traces of quinones which have been formed simultaneously, is found to contain two dibromo derivatives. That these two substances actually represent

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[4] Kogl and Erxleben, Ann., 479, 17, footnote (1930).

[5] Pummerer and Huppmann, Ber., 60, 1445 (1927).

the meso (V) and the racemic (VI) modifications of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone has been quite definitely established.

The two substances thus obtained differ from each other quite widely in melting point, 190–191 and 236–237°. Mixed melting points where less than 10% of the high-melting form is present, show values lower than the lower melting. The two compounds have a different solubility in various solvents.

Each of the two dibromohydroquinones can be acetylated to give its own perfectly stable characteristic diacetate (VII and VIII), and each of the diacetates can, in turn, be nitrated to the corresponding individual tetranitro compound (IX and X).

That the substances are actually stereoisomers and not simple isomers due to different positions of the two bromine atoms in each of the molecules, was proved in more than one way. Each of the two dibromohydroquinones could be oxidized to give the same dibromoquinone (XI). It would thus appear either that diphenyl isomerism cannot exist in the molecule when the quinone ring is present, or that, if it does exist, one form is so much more stable than the other that only one isomer of the corresponding quinones is actually isolated.

It is of interest to apply calculations based on x-ray data to this quinone in order to determine whether interference might be expected. If the assumptions are made that the internuclear distance between the linked carbon atoms of the benzene ring and the quinone ring is essentially the same as the distance between the linked carbon atoms of the two rings in diphenyl, and that the angles in the quinone ring are the same as in benzene, then the sum of the x-ray values for the $—C{=}O$ and the $C—CH_3$ should indicate the possibility or impossibility of resolution.[6] If the $C—CH_3$ is 1.73 Å. and the $C{=}O$ value is 1.15 Å. (merely the volume of the oxygen atom is taken here), and from their sum, 2.88 Å., the value 2.90 Å. (the distance between the linked carbon atoms in diphenyl) is subtracted, there is obtained a value of —0.02 Å. Thus the quinone oxygen and the methyl group of the benzene ring may be assumed not to collide and free rotation of the rings should be possible. Regardless of the proper explanation, the fact that identically the same compound is obtained by the oxidation of these two quite different hydroquinones, demonstrates quite positively the stereoisomeric nature of the two products.

Further evidence that these two dibromo compounds are of the type presented, and that both bromines are ortho to the hydroxyls in each molecule, was obtained. (1) The dibromoquinone (XI) from oxidation of either of the two pure hydroquinones gives upon reduction always a mixture of the high- and low-melting hydroquinones (V and VI). (2) The 3,6-di-(2,4-dimethylphenyl)-quinone (XII) from the oxidation of 3,6-di-(2,4-

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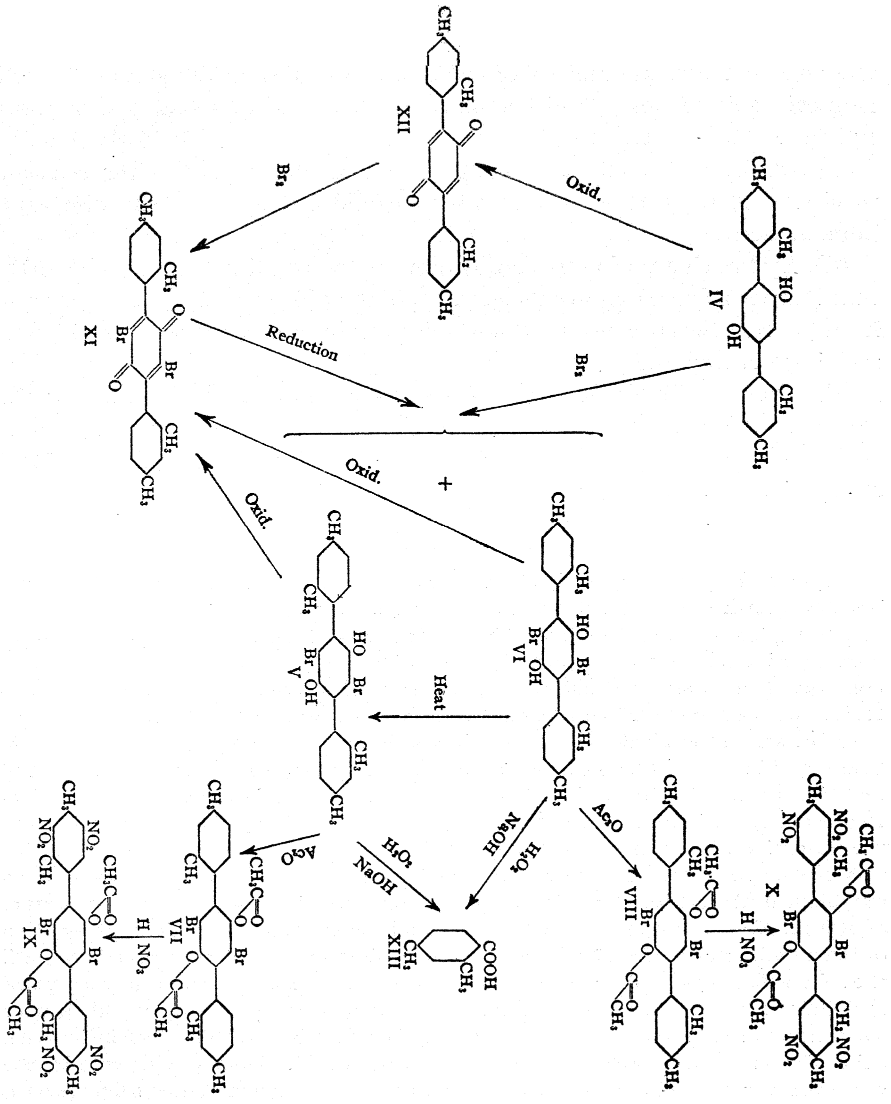
[6] Stanley and Adams, THIS JOURNAL, 52, 1200 (1930).

dimethylphenyl)hydroquinone (IV) can be brominated in chloroform to give the same dibromoquinone (XI) that is obtained by oxidation of the dibromohydroquinones.



(3) Each of the two dibromohydroquinones (V and VI) is oxidized by means of strong sodium hydroxide solution and hydrogen peroxide, presumably with the primary formation of the corresponding quinone which is then oxidized further to a benzene derivative. The final compound obtained in each case is 2,4-dimethylbenzoic acid (XIII). Unfortunately the

yields are lower than might be desired (about one mole per mole of original hydroquinone, whereas, theoretically, two moles are possible). However, in an oxidation of this sort it is not to be unexpected that a quantitative yield of product is not obtained. It is pertinent, however, that the dimethylbenzoic acid which is produced is essentially pure as it comes from the reaction mixture and this is true in the oxidation of each of the two isomeric substances. If either of the two compounds had one or more bromine atoms in either of the two end rings, it is extremely likely that the corresponding bromodimethylbenzoic acid would appear in the reaction product, at least to an extent which would contaminate the dimethylbenzoic acid.

(4) By heating the lower-melting dibromohydroquinone (m. p. 190–191°) to a temperature 30° above its melting point and holding it there for several hours, a reaction product results which contains a proportion of the higher-melting compound.

Whether the higher-melting dibromohydroquinone is the meso or the racemic modification has not as yet been determined. It should be possible to introduce a salt-forming group into the molecule and then through a study of the resolution characterize each substance.

Experimental Part

3,6-Di-(2,4-dimethylphenyl)-hydroquinone.—In a 1-liter, three-necked, round-bottomed flask equipped with a thermometer and very efficient stirrer was placed 375 cc. of m-xylene of b. p. 138–139°. The m-xylene was cooled to 5° and 140 g. of aluminum chloride added with stirring, after which 70 g. of pure, dry, powdered benzoquinone (purified by steam distilling crude product and then drying over phosphorus pentoxide) was added in portions of about 0.5 g. The reaction mixture immediately turned dark brown and gradually became so viscous that stirring was difficult. In order to insure rapid mixing of the solid quinone it was added at such a rate that most of it had been incorporated before the mixture became thick (about forty-five minutes). Efficient cooling to keep the temperature below 20° is necessary since above this point the formation of tar seems to be considerably increased. After the addition the stirring was continued for two hours and the dark brown reaction mixture allowed to stand overnight in the refrigerator. It was then poured with vigorous stirring into a mixture of 100 cc. of concentrated hydrochloric acid and 400 cc. of water. The decomposition of the aluminum chloride complex was somewhat slow and the mixture was stirred until the solid which separated was dark gray in color and the excess of m-xylene had separated in a definite layer. The solid was filtered by suction and dried in a vacuum desiccator over phosphorus pentoxide. The dark gray powdery product was dissolved in benzene. boiled for one hour with decolorizing charcoal and filtered. Upon cooling with ice the product separated as an amorphous powder which, upon recrystallization from benzene, came down in white microscopic needles. The yield was 30 g. (43.7% of the theoretical) of a product melting at 188–189°.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 82.97; H, 6.97. Found: C, 82.70; H, 6.76.

Stereoisomeric **3,6-Di-(2,4-dimethylphenyl)-2,5-dibromohydroquinones.**—In a 200-cc., three-necked, round-bottomed flask fitted with a dropping funnel, mercury-sealed stirrer **and** condenser with a trap for hydrogen bromide fumes were placed 13 g. (0.04

mole) of 3,6-di-(2,4-dimethylphenyl)-hydroquinone and 150 cc. of chloroform. The flask was warmed until the solid was completely dissolved, and the solution was then cooled to 40–50°. To this solution was added slowly with stirring 13 g. (0.08 mole) of bromine dissolved in 30 g. of chloroform (30% solution). The rate of addition was controlled so that the bromine was absorbed almost as rapidly as it entered the reaction mixture. After about three-fourths of the bromine had been added the temperature was raised to 70° to increase the rate of reaction. At this temperature fumes of hydrogen bromide were evolved for the first time; in experiments in which the entire bromination was carried out at 70°, however, the evolution of hydrogen bromide was continuous throughout the entire procedure.

The chloroform and slight amount of unreacted bromine were removed at once by distilling from a steam-bath under reduced pressure, adding more chloroform as required until the distillate was no longer colored with bromine. The chloroform was then distilled completely and to the dry, slightly yellow reaction product (amounting to 16-18 g.) was added 100 cc. of ethyl alcohol. If the bromination was properly controlled, the color was only slightly yellow (due to the presence of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromoquinone from oxidation of the hydroquinone). To the alcohol containing the partially dissolved product was added a few drops of hydrochloric acid and the minimum amount of stannous chloride required to decolorize the product. It is highly desirable to control the rate of addition of the bromine as indicated previously in the procedure so as to avoid oxidation and the use of stannous chloride as far as possible, since the latter seems to make the subsequent separation and purification of the two compounds in the product more difficult. The total yield of bromination product before crystallization was 16 g. (82% of the theoretical).

High-Melting Modification. a-Form.—The ethyl alcohol containing the partially dissolved bromination product and stannous chloride was boiled until completely decolorized, cooled somewhat and filtered by suction. The residue was recrystallized from acetone until it reached a constant melting point at 236–237°. The yield was 6 g. of white hexagonal prisms.

Anal. (Parr Bomb) Calcd. for $C_{22}H_{20}O_2Br_2$: Br. 33.61. Found: Br, 33.5.

Low-Melting Modification. β-Form.—The filtrate from the ethyl alcohol treatment of the bromination product of 3,6-di-(2,4-dimethylphenyl)-hydroquinone was cooled in an ice-bath for about two hours, during which time a small quantity of white crystals separated. This was filtered and 1.5 g. of a product was obtained melting without recrystallization at 130-131° which proved to be the high-melting modification contaminated with a small amount of the low-melting compound. The filtrate was evaporated to dryness at room temperature under reduced pressure. The slightly yellow product was recrystallized from acetone. Repeated crystallization from both acetone and methyl alcohol gave a product having a constant melting point of 190-191°. The yield was 4 g. of white tetragonal prisms.

Anal. Calcd. for $C_{22}H_{20}O_2Br_2$: Br, 33.61. Found: Br, 33.5.

The melting of a mixture of 5% 236-237' compound with 95% 190–191° compound showed softening at 181° and melting at 184–189°.

The solubility of the low- and high-melting compounds is markedly different. The compound melting at 236-237' is only slightly soluble in hot ethyl alcohol while the compound melting at 190-191' can be induced to crystallize from its solution in ethyl alcohol only by evaporation and cooling. A difference, though not so great, is found in methyl alcohol and acetone.

The successful isolation of the high- and low-melting compounds in the pure state depends upon the initial separation by the use of ethyl alcohol as described in the above procedure. If too much alcohol is used, the low-melting compound is contaminated with the high-melting product and is purified by subsequent recrystallization only with great difficulty and loss of material in the filtrates. If too little alcohol is used the high-melting compound will be contaminated with the other form, but this product is more easily purified, at least to a point a few degrees below the correct melting point.

One attempt was made to carry out a fractional crystallization of the crude bromination product using methyl alcohol as the solvent and omitting the preliminary separation with ethyl alcohol. The different fractions obtained after several crystallizations seemed from their melting points to be mixtures of various proportions of the more and less soluble modifications.

3,6-Di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone Diacetate. **α-Form.** A. (Derivative of Hydroquinone Melting at 236–237°.)—Six grams of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone was dissolved in 10 cc. of hot pyridine and 12 cc. of acetic anhydride added with stirring. The solution was heated almost to boiling for fifteen minutes, after which time the acetyl derivative began to separate from the hot solution. The reaction mixture was cooled with ice and allowed to stand for several hours, after which the product was filtered, recrystallized from acetic anhydride and left in a vacuum desiccator until the odor of acetic anhydride could no longer be detected. The yield was 6 g. of hard, white, orthorhombic crystals melting at 235–236°. Only a small amount of additional material was obtained by pouring the original pyridine–acetic anhydride filtrate into water. This acetyl derivative is only slightly soluble in hot acetone.

Anal. Calcd. for $C_{26}H_{24}O_4Br_2$: Br, 28.57. Found: Br, 28.29.

3,6-Di-(2,4-dimethyl-3,5-dinitrophenyl)-2,5-dibromohydroquinone Diacetate. α-Form.—To 40 cc. of fuming nitric acid (sp. gr. 1.48) coaled below −5° was addedslowly with very rapid stirring 6 g. of the powdered diacetyl derivative just previously described and melting at 235–236°. A red coloration appeared momentarily as the solid came in contact with the acid but disappeared as the compound went into solution. After standing in the freezing mixture for 15 minutes a solid began to separate, and after one hour the nitration mixture was poured into ice water. The nitro derivative was filtered, washed free of acid with a 5% sodium carbonate solution, followed by water and dried. The product was washed with acetone until pure white and melted at 304–305° after drying. Crystallization from acetic anhydride yielded 4.8 g. of white needles melting sharply at 305–306° (decomposed after melting, with evolution of gas bubbles).

Anal. (Parr Bomb) Calcd. for $C_{26}H_{20}O_{12}N_4Br_2$: Br, 21.62. Found: Br, 21.78.

3,6-Di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone Diacetate. **β-Form.** B. (Derivative of Hydroquinone Melting at 190–191°.)—The acetylation was carried out in the same way as for the acetylation of the high-melting hydroquinone using 4 g. of the substituted hydroquinone, 5 cc. of pyridine and 8 cc. of acetic anhydride. The acetyl derivative did not separate from the hot solution as in the previous case, but came out on cooling in an ice–salt mixture. It was allowed to stand overnight and the white powdery product filtered by suction. The amount thus obtained was 3.5 g. and 1 g. additional by pouring the filtrate into water. The product was readily soluble in acetone as contrasted with the preceding diacetyl derivative, and upon recrystallization from this solvent yielded 3 g. of white microscopic needles melting at 193–194° (with previous softening). A mixed melting point with the starting material showed a depression and melted over a range of 160–165°.

Anal. Calcd. for $C_{26}H_{24}O_4Br_2$: Br, 28.57. Found: Br. 28.42.

3,6-Di-(2,4-dimethyl-3,5-dinitrophenyl)-2,5-dibromohydroquinone Diacetate. *B*-Form.—The nitration of the diacetate just described was carried out as in the case of the higher-melting diacetate using 2 g. of the diacetyl derivative and 20 cc. of fuming nitric acid. The product in this case did not precipitate from the cold nitration mixture even after long standing, and it was found more satisfactory to pour the solution immediately into ice water in order to avoid excessive formation of a lemon-yellow by-product, presumably formed by hydrolysis of the acetyl groups, followed by oxidation. Recrystallization from acetone yielded 0.4 g. of microscopic white needles melting at 282–283° with slight decomposition and evolution of gas.

Anal. Calcd. for $C_{26}H_{20}O_{12}N_4Br_2$: Br, 21.62. Found: Br, 21.43.

3,6-Di-(2,4-dimethylphenyl)-2,5-dibromoquinone.—Oxidation of the substituted hydroquinones to the corresponding quinones was carried out most readily by the method of Pummerer,[5] using benzoquinone as the oxidizing agent.

One gram of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone was dissolved in the minimum amount of hot methyl alcohol and 0.1 g. of benzoquinone added. The solution turned orange almost at once, and was boiled for ten minutes, during which time the less soluble substituted quinone began to precipitate. Another 0.1-g. portion of benzoquinone was added, the reaction mixture boiled for ten minutes and then cooled with ice. The product was filtered, recrystallized from methyl alcohol and dried in a vacuum desiccator; yield, 0.7 g. of microscopic orange needles melting at 197–198°.

Anal. Calcd. for $C_{22}H_{18}O_2Br_2$: Br, 33.75. Found: Br, 33.60.

One gram of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone (m. p. 236–237°) was oxidized as in the preceding experiment, and yielded 0.8 g. of orange needles melting at 198° after one recrystallization from methyl alcohol. Repeated crystallization failed to raise the melting point.

A mixed melting point of the quinones obtained from the 190–191° and 236–237° compounds showed no depression.

3,6-Di-(2,4-dimethylphenyl)-quinone and **3,6-Di-(2,4-dimethylphenyl)-2,5-dibromoquine.**—3,6-Di-(2,4-dimethylphenyl)-quinone was prepared from the corresponding hydroquinone by the oxidation procedure given in the preceding experiment. The product, after crystallization from methyl alcohol, from 2 g. of hydroquinone was 1.8 g. of reddish-brown crystals melting at 180°.

The 1.8 g. of 3,6-di-(2,4-dimethylphenyl)-quinone was dissolved in 50 cc. of chloroform and a 30% solution of 2 g. of bromine in chloroform was added slowly with stirring at room temperature. The bromine was absorbed instantly but no hydrogen bromide was evolved until the solution was warmed. The chloroform was distilled, leaving 4 g. of an orange, crystalline product. Upon dissolving the material in methyl alcohol it was observed that some white crystalline substance was present, possibly some substituted hydroquinone formed by the addition of hydrogen bromide to the quinone. The solution was, therefore, treated with benzoquinone and boiled, after which an orange product separated which resembled in appearance the dibromoquinones previously prepared. After repeated crystallization from methyl alcohol, there was obtained 2 g. of an orange product melting sharply at 198°. A mixed melting point with 3,6-di-(2,4-dimethylphenyl)-2,5-dibromoquinone prepared by the other method described showed no depression.

Reduction of **3,6-Di-(2,4-dimethylphenyl)-2,5-dibromoquinone.**—A solution of 3.8 g. of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromoquinone in acetone was reduced by means of 1.5 g. of stannous chloride and 2 cc. of concentrated hydrochloric acid. Decolorization of the orange solution was almost immediate after slight warming. The solution was poured into four times its amount of water and the precipitated reduction product filtered, washed several times with water and dried. To the product was added 40 cc. of ethyl alcohol; the mixture was heated for five minutes and filtered while warm. The insoluble part amounting to 1.2 g. was recrystallized from acetone to constant melting point and yielded 1.1 g. of a compound melting at 236–237°. The filtrate was cooled and permitted to stand for one hour, after which the crystals that had separated were filtered. Four-tenths of a gram of high-melting compound contaminated with some of the low-melting modification was thus obtained. It melted at 230–232° (softens at 225°). The acetone filtrate was evaporated to dryness at ordinary temperature and under reduced pressure and yielded 1.3 g. of substance melting at 190–192° (softens at 187°). This, after recrystallization from acetone, yielded 0.8 g. of a compound melting constantly at 190–191°. The compounds have also been purified in other experiments by crystallization from methyl alcohol.

Stability to Heat of 3,6-Di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone, m. p. 190–191°.—In a small bomb tube was placed one gram of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone (m. p. 190–191°) and the tube evacuated to 10 mm. The tube was then filled with nitrogen, again evacuated and the process repeated several times to insure complete removal of oxygen. The bomb tube was then sealed off while filled with nitrogen and immersed in an oil-bath at 220°, whereupon the substance melted to a clear liquid. After one hour (longer heating is not possible because of decomposition) the tube was allowed to cool to room temperature, after which it was opened and the white solidified product heated with 15 cc. of ethyl alcohol. The residue insoluble in alcohol was filtered and crystallized from acetone. There was thus obtained 0.05 g. of white crystals melting at 235–236°. A mixed melting point with the high-melting modification showed no depression.

Oxidation of 3,6-Di-(2,4-dimethylphenyl)-2,5-dibromoquinone to 2,4-Dimethylbenzoic Acid.—One gram of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromoquinone was suspended in 50 cc. of 20% sodium hydroxide solution and 25 cc. of 30% hydrogen peroxide added with stirring. The quinone gradually dissolved and the original deep red color of the solution changed to pink in the course of six hours. The addition of 25 cc. more of hydrogen peroxide and longer stirring failed to effect further change. The solution, in which the odor characteristic of aromatic aldehydes was noticeable, was acidified and the yellow solid which precipitated was filtered and dried. It was redissolved in very dilute sodium hydroxide and the pink color reappeared. Upon addition of 10 cc. of hydrogen peroxide to this faintly alkaline solution, a vigorous reaction occurred and the solution became decolorized in a few minutes. Acidification with hydrochloric acid caused the precipitation of a fairly white product. This was extracted with ether, the ether solution shaken out with a saturated sodium bicarbonate solution, and this alkaline solution acidified with hydrochloric acid. The product precipitated and was filtered and recrystallized from dilute ethyl alcohol. The yield was 0.2 g. of a compound melting sharply at 125–126°. A mixed melting point with 2,4-dimethylbenzoic acid showed no depression.

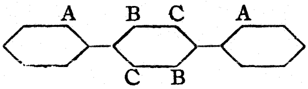
Neut. Equiv. Subs., 0.0788 g.: 0.1015 *N* NaOH, 5.07 cc. Calcd. for C_8H_9COOH: mol. wt., 150. Found: mol. wt. 153.

Oxidation of 3,6-Di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone (m. p. 190–191°) to 2,4-Dimethylbenzoic Acid.—The oxidation was carried out in the same way as in the preceding experiment using 0.25 g. of the substituted hydroquinone, 30 cc. of 20% sodium hydroxide and 25 cc. of 30% hydrogen peroxide. The yield after the various extractions and purification was 0.06 g. (*i. e.*, 0.7 mole of acid from 1 mole of the compound) of 2,4-dimethylbenzoic acid melting at 125–126°.

Oxidation of 3,6-Di-(2,4-dimethylphenyl)-2,5-dibromohydroquinone (m. p. 236–237°) to 2,4-Dimethylbenzoic Acid.—The oxidation was accomplished as before, using 0.47 g. of substance, 50 cc. of 20% sodium hydroxide solution, and 50 cc. of 30% hydrogen peroxide. The 2,4-dimethylbenzoic acid was isolated and purified as before, and amounted to 0.13 g. (0.8 mole of acid from 1 mole of substance). The melting point was 125–126°.

Summary

1. Two stereoisomeric 3,6-di-(2,4-dimethylphenyl)-2,5-dibromodihydroquinones and some derivatives have been prepared.
2. These substances are the racemic and the meso modifications of a molecule of the following type



3. It may be concluded that the same conditions which cause optical isomerism in the diphenyl series also exist in the terphenyl series.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS WELLCOME AND COMPANY]

MIXED BENZOINS. II

BY JOHANNES S. BUCK AND WALTER S. IDE

RECEIVED JULY 26, 1930 PUBLISHED OCTOBER 6, 1930

In continuation of the work described in Part I,[1] six new benzoins, together with their benzils and desoxy compounds have been prepared. The work described cannot be said to support, or detract from, the theoretical conclusions advanced in Part I, as data on the reactivity of the aldehydes are lacking. The benzoins described in the present paper were all prepared in the usual manner, by mixing the reactants and refluxing, as it was found that the technique earlier described gave little, if any, better yields in the present cases. The results described in Part I and Part II represent the best that can be obtained by fractionation methods, and it is evident that further knowledge can only be attained by complete analysis of the reaction mixtures. It is hoped to carry this out in some cases.

Attention was given to the possibility of the occurrence of isomeric mixed benzoins, but no examples were found. Their occurrence, however, is not excluded, as in general only about one-half of the reactants was accounted for. The mixed benzoins described are very probably individuals and not mixtures or addition compounds, as in each case only one desoxy compound was obtained on reduction.

The mixed benzoins described are not specifically named, as it is not possible to assign either of the two alternative structures with any degree of probability,

Experimental

Benzoin from *p*-Dimethylaminobenzaldehyde and Anisaldehyde, (A).—Seven and one-half grams of *p*-dimethylaminobenzaldehyde, and 7.0 g. of anisaldehyde, dis-

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[1] Buck and Ide, THIS JOURNAL, 52,220 (1930).

solved in 50 cc. of 50% alcohol, were refluxed for two and one-half hours with 4.0 g. of potassium cyanide. The product, recrystallized from alcohol, forms white flakes, moderately soluble in alcohol and very soluble in ether, benzene and ligroin; yield 52%. The product melts at 144° (uncorr.).

Anal. Calcd. for $C_{17}H_{19}O_3N$: N, 4.91. Found: N, 4.67.

Benzoin from *p*-Chlorobenzaldehyde and Piperonal, (B).—This benzoin was prepared by refluxing a solution of 3.5 g of p-chlorobenzaldehyde, 3.8 g. of piperonal and 5.0 g. of potassium cyanide in 50 cc. of 50% alcohol for two hours. The yield was 40%. On recrystallization from alcohol the compound forms yellow needles melting at 110° (uncorr.). It is moderately soluble in alcohol, very soluble in ether and chloroform and slightly soluble in benzene and ligroin.

Anal. Calcd. for $C_{15}H_{11}O_4Cl$: C, 61.95; H, 3.79. Found: C, 61.81; H, 3.68.

Benzoin from o-Chlorobenzaldehyde and Anisaldehyde, (C).—Seven grams of o-chlorobenzaldehyde, 6.8 g. of anisaldehyde and 4.0 g. of potassium cyanide, dissolved in 75 cc. of 50% alcohol, were refluxed for two hours. On standing crystals separated. After recrystallization from alcohol, the compound forms colorless, hexagonal crystals, melting at 84° (uncorr.). It is moderately soluble in alcohol and ligroin and very soluble in benzene, ether and chloroform; yield 60%.

Anal. Calcd. for $C_{15}H_{13}O_3Cl$: Cl, 12.83. Found: Cl, 12.72.

Benzoin from o-Chlorobenzaldehyde and Veratric Aldehyde, (D).—A solution of 8.3 g. of veratric aldehyde, 7.0 g. of o-chlorobenzaldehyde and 4.0 g. of potassium cyanide in 75 cc. of 50% alcohol was refluxed for two and one-half hours. On cooling the product crystallized out. After recrystallization from alcohol the compound forms fine white needles, melting at 140° (uncorr.). It is moderately soluble in alcohol, ligroin and benzene and very soluble in ether and chloroform; yield 70%.

Anal. Calcd. for $C_{16}H_{15}O_4Cl$: Cl, 11.57. Found: Cl, 11.31).

Benzoin from m-Chlorobenzaldehyde and p-Dimethylaminobenzaldehyde, (E).—The compound was prepared by refluxing, for two hours, a solution of 7.0 g. of *m*-chlorobenzaldehyde, 7.5 g. of *p*-dimethylaminobenzaldehyde and 4.0 g. of potassium cyanide in 75 cc. of 50% alcohol. After recrystallization from alcohol, the benzoin forms either large dark brown rhombs, or small yellow rhombs, both forms melting at 140° (uncorr.) and showing no depression when mixed. On reduction both gave the same desoxy compound. The compound is moderately soluble in benzene, alcohol and ether, slightly soluble in ligroin and very soluble in chloroform: yield 45%.

Anal. Calcd. for $C_{16}H_{16}O_2NCl$: Cl, 12.24. Found: Cl, 11.98.

Benzoin from m-Bromobenzaldehyde and Anisaldehyde, (F).—Seven grams of anisaldehyde, 9.3 g. of *m*-bromobenzaldehyde and 4.0 g. of potassium cyanide. dissolved in 50 cc. of 50% alcohol, were refluxed for two and one-half hours. The oil which separated was crystallized from alcohol. After recrystallization the compound forms yellow cubes, melting at 88° (uncorr.). It is moderately soluble in alcohol, benzene, ether and ligroin and very soluble in chloroform: yield 20%.

Anal. Calcd. for $C_{15}H_{13}O_3Br$: C. 56.04; H, 4.08. Found: C, 55.79; H, 3.91.

It should be pointed out that in the preparation of some mixed benzoins considerable patience is necessary to induce crystallization of the crude products, prolonged exposure of the solutions to temperatures around 0° sometimes being required. The authors have obtained clear indications of the formation of a number of other mixed benzoins but as yet have not succeeded in isolating sufficient crystalline material to justify descriptions of the experiments.

Benzil Derivatives.—The mixed benzoin (usually 2.0 g. was taken) dissolved in alcohol was oxidized with a slight excess of Fehling's solution and recrystallized from alcohol until pure. There is, of course, no ambiguity in the structure. The benzils are tabulated in Table I.

TABLE I

BENZIL DERIVATIVES

Formula	Benzoin	M. p., °C.	Yield, %	Appearance	Analysis, %	Calcd.	Found
$Me_2NC_6H_4COCOC_6H_4OMe$	A	128	85	Yellow hexagons	N	4.94	4.79
p-$ClC_6H_4COCOC_6H_3O_2H_2C$	B	132	78	Fine yellow needles	C	62.38	62.24
					H	3.12	2.99
o-$ClC_6H_4COCOC_6H_4OMe$	C	104	70	Yellow rhombs	Cl	12.92	13.02
o-$ClC_6H_4COCOC_6H_3(OMe)_2$	D	117	85	Yellow rhombs	C	63.04	63.00
					H	4.31	4.40
m-$ClC_6H_4COCOC_6H_4NMe_2$	E	130	90	Slender amber plates	C	66.77	66.53
					H	4.91	5.21
m-$BrC_6H_4COCOC_6H_4OMe$	F	94	88	Fine yellow needles	C	56.42	56.22
					H	3.48	3.62

TABLE II

DESOXY COMPOUNDS

Formula	Benzoin	M. p., °C.	Yield, %	Appearance	Analysis, % Calcd. C	Calcd. H	Found C	Found H
$C_{17}H_{19}O_2N$	A	130	88	White flakes	75.79	7.06	75.50	7.33
$C_{15}H_{11}O_3Cl$	B	113	80	White needles	65.56	4.01	65.72	4.09
$C_{15}H_{13}O_2Cl$	C	96	85	White prisms	69.08	5.03	69.00	4.91
$C_{16}H_{15}O_3Cl$	D	110	80	White needles	66.07	5.20	66.44	5.26
$C_{16}H_{16}ONCl$	E	125	80	White needles	70.18	5.89	69.90	5.99
$C_{15}H_{13}O_2Br$	F	54	86	Fine white flakes	59.01	4.30	58.82	4.24

Desoxy Compounds.—These were prepared in general by refluxing 2.0 g. of mixed benzoin, 3 cc. of concentrated hydrochloric acid, 10 cc. of alcohol and 2.0 g. of tin with a trace of copper sulfate for five to six hours. The product was then crystallized from alcohol. The structure naturally depends on that of the parent benzoin and at present it is not possible to decide between the two alternative structures. Only one desoxy compound was obtained from each benzoin, indicating that the latter was a definite compound, not a mixture of two isomers (see Table II).

Summary

In continuation of previous work, six new mixed benzoins have been isolated and their benzils and desoxy compounds prepared.

TUCKAHOE, NEW YORK

[CONTRIBUTION NO. 40 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY]

STUDIES ON POLYMERIZATION AND RING FORMATION. VI. ADIPIC ANHYDRIDE

BY JULIAN W. HILL

RECEIVED JULY 26, 1930 PUBLISHED OCTOBER 6, 1930

The anhydrides of succinic and glutaric acids are known and are monomeric rings of five and six atoms, respectively. The monomeric anhydride of the next member of the series, adipic acid, is a seven-atom ring, and therefore the direct preparation of this anhydride by the removal of water from the acid should give a polymolecular product, in accordance with the generalizations formulated in the previous papers in this series.[1] This has been found to be the case. We have. also been successful in preparing monomeric adipic anhydride for the first time.

Adipic anhydride has been prepared by Voerman[2] and by Farmer and Kracovski,[3] both of whom describe it as a solid. Voerman prepared the compound by treating adipic acid with acetyl chloride, removing volatile compounds in *vacuo*, and finally crystallizing from benzene. He gives a melting point of 98°. On the basis of a molecular weight determination in phenol, with which, however, we have found it to react, he seemed to regard the compound as a monomeric ring. The abnormally high molecular weight obtained in boiling acetone, the lack of definite crystallinity, and the relatively low solubility of the compound, however, led him to consider that it might be polymeric. He does not make his viewpoint altogether clear, but apparently he regarded the anomalous properties of the compound as due to some sort of association of simple rings and did not consider the probability of the existence of a long chain or large ring.

Farmer and Kracovski state that adipic anhydride is definitely unimolecular and ascribe to it a melting point of 97°. This is certainly not correct since we have found the monomer to melt at a very much lower temperature.

We have prepared adipic anhydride by both of these methods and have found that the product before subjection to distillation is polymeric, as we had anticipated and Voerman suspected. Polymeric adipic anhydride separates from hot benzene as a microcrystalline powder. Samples prepared in various experiments showed melting points ranging from 70 to 85°. This variation and the difference between the melting points of our products and those of previous investigators may be due to differences in molecu-

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[1] Carothero, THIS JOURNAL, 51, 2548 (1929); Carothers and Arvin, *ibid.*, 51, 2560 (1929); Carothers and Van Natta, *ibid.*, 52, 314 (1930); Carothers and Dorough, *ibid.*, 52, 711 (1930).

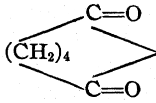
[2] Voerman, *Rec. trav. chim.*, 23, 265 (1904).

[3] Farmer and Kracovski, *J. Chem. Soc.*, 680 (1927).

lar size. A molecular weight determination in boiling benzene gave a value about six times the normal value. This value is probably low as the substance is very sensitive to moisture, and only the ordinary precautions were taken to exclude it. The compound hydrolyzes in boiling water to yield the acid and reacts rapidly with aniline and phenol. It is hygroscopic and on standing unprotected gradually reverts to the acid. It is not distillable as such, but when heated in *vacuo* to somewhat above 200°, it breaks down and yields the true monomeric adipic anhydride, which distils out.

Monomeric adipic anhydride is a liquid freezing at about 20° and boiling at about 100° at 0.1 mm. It reacts with cold water quickly with the evolution of much heat to yield the acid. It reacts almost instantly with aniline to give a very high yield of pure monoanilide. On being heated at 100° for a few hours, it changes to a polymer melting at 80–85°. On standing at room temperature for ten days or more, it gradually solidifies. It is probable that traces of water bring about the polymerization. When a sample of liquid anhydride is transferred to a vessel which has not been very carefully dried, an amorphous skin soon coats the glass.

The reactions of the monomeric and polymeric adipic anhydrides with aniline establish the structures of these compounds, the former as a seven-membered ring and the latter as a long chain, which may be a large ring or an open chain with terminal carboxyl groups. Monomeric anhydride (I), which has a symmetrical structure, can react with aniline to give but one product, adipic acid monoanilide (II). This has been verified experimentally. Polymeric adipic anhydride, to which we may assign formula III, on the other hand, is no longer symmetrical as soon as one anhydride group reacts with aniline. The product formed, therefore, depends on which side of the oxygen atom the next anhydride group along the chain breaks. It will be seen from the scheme above that the reaction of polymeric adipic anhydride with aniline may lead to three products: adipic acid, adipic acid monoanilide and adipic acid dianilide. All of these compounds have been isolated from the reaction of the polymer with aniline.



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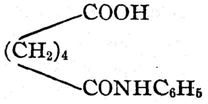
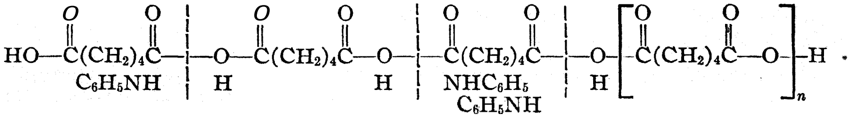


II



$$\mathrm{HO{-}\overset{\displaystyle O}{\overset{\|}{C}}(CH_2)_4\overset{\displaystyle O}{\overset{\|}{C}}{-}\underset{C_6H_5NH}{|}{-}\underset{H}{O}{-}\overset{\displaystyle O}{\overset{\|}{C}}(CH_2)_4\overset{\displaystyle O}{\overset{\|}{C}}{-}\underset{H}{O}{-}|{-}\overset{\displaystyle O}{\overset{\|}{C}}(CH_2)_4\overset{\displaystyle O}{\overset{\|}{C}}{-}\underset{NHC_6H_5}{|}{-}\underset{H}{O}{-}\left[\overset{\displaystyle O}{\overset{\|}{C}}(CH_2)_4\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}\right]_n{-}H}$$

$$\mathrm{C_6H_5NH}$$

III

On the assumption that a random reaction takes place and that the carboxyl groups which are probably at the ends of the chain may be neglected, these products should be formed in the proportion of one mole of acid to one mole of dianilide to two moles of monoanilide. In a quantitative experiment a 25% yield of dianilide was obtained. The adipic acid and monoanilide formed were not estimated quantitatively. Similarly the solid anhydride yields diphenyl adipate on warming with phenol.

The experiments with aniline show definitely that the solid adipic anhydride is a true condensation polymer in which the structural units are held together by primary valence forces. It is presumed that the polymers are open chains with carboxyl groups at the ends as has been demonstrated in the case of some of the polymeric ethylene succinates.[4] This view is further supported by the presence of adipic acid in the distillate when the polymeric anhydride is cracked to form the monomer.

The writer wishes to thank Dr. W. H. Carothers for his interest and advice, and Mr. S. B. Kuykendall for determinations of carbon and hydrogen.

Experimental Part

Preparation of Polymeric Adipic Anhydride.--One hundred grams of recrystallized adipic acid and 300 cc. of redistilled acetic anhydride were refluxed together for four to six hours, and the volatile constituents were removed in a vacuum at 100°. The residue melted at about 70°. It was repeatedly recrystallized from dry benzene, from which it separated as a micro-crystalline powder. Various samples prepared in this same way melted at temperatures varying from 70 to 85°. At temperatures above the melting point, all these samples were viscous liquids, which solidified on cooling to waxy masses. In all experiments moisture was carefully excluded. In the most careful preparation carried out, moisture was excluded by phosphorus pentoxide tubes, the residue was heated overnight in an exhausted system which contained caustic potash in an adjacent vessel and then recrystallized four times with one filtration in a closed system. After each recrystallization the mother liquor was removed by careful decantation. The product melted at 73-75°. The polymeric anhydride melted under boiling water and gradually went into solution. On cooling adipic acid crystallized out.

Anal. Calcd. for $(C_6H_8O_3)_n$: saponification equiv., 64.0. Found: saponification equiv., 63.2, 63.4.

Reaction of Polymeric Adipic Anhydride with Aniline.—A sample of polymer prepared directly from adipic acid and acetic anhydride (m. p. 75°) was added to a slight excess of aniline and triturated in a mortar. Reaction took place spontaneously with the evolution of heat. The mixture was treated with dilute hydrochloric acid and the solid precipitate was filtered off. The filtrate was evaporated to dryness and the residue was then taken up in a volume of water not quite sufficient for complete solution, filtered and washed. The residue after crystallization from water was identified as adipic acid by a mixed melting point determination. The residue from the hydrochloric acid treatment was boiled with water and filtered. The filtrate deposited needles on cooling, which, after recrystallization from water, were identified as adipic acid monoanilide by a mixed

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[4] Carothers and Dorough, This Journal, 52, 711 (1930).

melting point with an authentic sample, The residue insoluble in boiling water, consisting of adipic acid dianilide, was recrystallized from alcohol; needles, m. p. 240–241°.[5] This experiment was carried out with various samples of polymeric anhydride: crude polymer prepared directly from adipic acid and acetic anhydride, recrystallized polymer, polymer formed by heating the monomer, and still-residue from distillation of the monomer. In every case dianilide was isolated and identified. The experiment with the heat polymer was carried out quantitatively and gave a 25% yield of dianilide.

Anal. Calcd. for $C_{18}H_{20}O_2N_2$: C, 72.96; H, 6.81. Found: C, 73.31, 73.24; H, 6.95, 7.12.

Reaction of Polymeric Adipic Anhydride with Phenol.—Polymeric adipic anhydride was warmed with phenol to fusion and poured into cold water. On agitation a white solid separated out. This, after two recrystallizations from a mixture of alcohol and water (1:1), separated as lustrous plates of m. p. 105.5–106°. The method of preparation and the ultimate analysis showed this compound to be diphenyl adipate.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.45; H, 6.08. Found: C, 72.63, 72.19; H, 6.07, 6.29.

Preparation of Monomeric Adipic Anhydride.—One hundred grams of adipic acid and 300 cc. of acetic anhydride were refluxed together for four hours. The acetic acid formed in the reaction and the excess acetic anhydride were removed by distillation in a vacuum. The residue was transferred to a Claisen flask and heated under vacuum. After the removal of the residual acetic anhydride at 0.1 mm. no further distillation took place up to 210° bath temperature. At this temperature the pressure rose, and in different experiments from 50 to 60 g. distilled between 105 and 125" under pressure from 3 to 8 mm., the bath temperature ranging from 210 to 235°. The residue was viscous when hot and solidified to a dark colored mass on cooling. The distillate consisted of a light pink liquid containing a small amount of crystalline material. The liquid and solid phases were separated by centrifuging. The crystalline material was washed with benzene, recrystallized from ethyl acetate, and identified as adipic acid by a mixed melting point determination. The liquid was redistilled in an all-glass apparatus. The boiling point was 98 to 100° at 0.1 mm. at a bath temperature of 117 to 120°. Only about half of the material could be recovered by distillation since the residue gradually polymerized. Samples of the colorless distillate were sealed in small, carefully dried glass tubes for freezing point determinations. The compound froze at 19° to large translucent plates and remelted at 22°.

Anal. Calcd. for $C_6H_8O_3$: C, 56.25; H, 6.30; mol. wt., 128; saponification equiv., 64.0. Found: C, 55.89, 55.98; H, 6.51, 6.52; mol. wt. (in boiling benzene), 134, 131; saponification equiv., 63.7, 63.6.

Polymerization of Monomeric Adipic Anhydride.—When monomeric adipic anhydride was transferred to a vessel which had not been carefully dried, a translucent coating appeared on the surface of the glass. The coating was amorphous and in places skin-like. It melted at 60–65°. When the liquid was heated in a sealed tube at 100°, it polymerized completely and a maximum melting point of 80–84° was reached in about seven hours. On being heated at 138°, a maximum melting point of 81–85" was reached in about two hours. In neither experiment did further heating affect the melting point.

Anal. Calcd. for $(C_6H_8O_3)_n$: saponification equiv., 64.0. Found: saponification equiv., 63.5, 63.3; mol. wt. (in boiling benzene), 860, 710.

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[5] Bodtker [*Ber.*, 39, 2765, 4003 (1906)] gives 240°; Balbiano [*Gazz. chim. ital.*, 32, *I*, 446 (1902)] gives 240–241°; Bouveault and Titry [*Bull. soc. chim.*, [3] *25*, 444 (1901)] gives 235°.

Reaction of Monomeric Adipic Anhydride with Aniline.—One cubic centimeter of anhydride was added to about eight cubic centimeters of aniline with stimng. Reaction was immediate and much heat was evolved. The excess aniline was dissolved in dilute hydrochloric acid. The solution was diluted to 200 cc. and filtered. The crude product was dried and weighed; m. p. 152–153°; yield 80%. The monoanilide of adipic acid has previously been prepared by heating $C_6H_5NHCOCH(COOH)(CH_2)_3COOH$.[6] Recrystallization from water did not raise the melting point. The crude compound was completely soluble in hot water (absence of dianilide). A similar experiment was carried out and worked up in smaller volume; m. p. (crude), 151–153°; yield, 87%.

Anal. Calcd. for $C_{12}H_{15}O_3N$: C, 65.12; H, 6.80; neutralization equiv., 221. Found: C, 64.76, 64.86; H, 6.81, 7.01; neutralization equiv., 222,223.

Summary

The monomeric and polymeric forms of adipic anhydride have been prepared, the former for the first time, and they have been shown to be mutually interconvertible. The reactions of the compounds with aniline have shown the monomer to be a seven-atom ring and the polymer a long chain or large ring. Diphenyl adipate is described.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

BRAZIL NUT OIL

BY H. A. SCHUETTE, RALPH W. THOMAS AND MABEL DUTHEY

RECEIVED JULY 28, 1930 PUBLISHED OCTOBER 6, 1930

Data pertinent to the composition of the oil in the seeds of the Brazil nut tree, *Bertholletea excelsa,* are few. A statement by Andes[1] that this oil consists of stearin, palmitin and olein, and several reports by others[2] on a few of its more common chemical and physical constants appear to represent the published information on its chemical composition.

This oil finds a limited use in the arts in this zone but in the country of its origin it serves the inhabitants much the same as olive oil does elsewhere, that is, for alimentary purposes, for soapmaking and, to some extent, as a fuel for lamps. The nut meats contain approximately 70% of oil, more than one-half of which may be removed merely by expression in a hand press.

In view of the situation which obtains as above noted, and the ambiguity surrounding the methods of recovery of the oil used by others, it seemed worthwhile to re-investigate the chemical and physical characteristics of

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[6] Dieckmann, *Ann.*, **317**, 62 (1901). *The* melting point given is 152–153°.

[1] Andes, "Vegetable Fats and Oils" (translated by Salter), Scott, Greenwood and Co.. London, 1902, p. 187.

[2] De Negri and Fabris, *Z. anal. Chem.*, 33, 563 (1894); De Negri, *Chem.-Ztg.*, 22, 961 (1898); Merrill, *Maine* Agr. *Expt. Sta. Bull.*, 65, 111 (1900); Grimme, *Analyst*, 36, 21 (1911); Niederstadt, *Ber. deut. pharm. Ges.*, 35, 145 (1902).

both the expressed product and that recoverable from the residues by solvent extraction, and to make an analysis of the latter. The presentation of these data is the object of this communication.

I. Preparation of Materials

The oil in the meats[3] from twelve kg. of fresh Brazil nuts was expressed in a small, manual press rather than one of the hydraulic type because it had been demonstrated by experimental trials that a cleaner product and one better adapted for chemical analysis without a preliminary refining process is obtainable by using this method of recovery. The residual meat pulp was then extracted in percolators with low-boiling petroleum ether, the final portions of which were in turn removed from the oil in the presence of carbon dioxide. A dark brown oil was recovered from which, in distinction to that obtained by expression, no glycerides separated when stored in the refrigerator (5–10°). The expressed oil possessed, after filtration, a pale yellow color and a taste suggestive of the nut itself.

II. Analysis of Oils

(a) Chemical and Physical Characteristics.—The more important chemical and physical characteristics (Table I) of both the expressed oil and that recovered from the residual meat pulp were determined by recog-

TABLE I

CHEMICAL AND PHYSICAL CHARACTERISTICS OF BRAZIL NUT OIL

	Expressed oil	Residual oil
Specific gravity 25°/25°	0.9150	0.9143
Index of refraction 20°	1.4678	1.4683
Titer test	...	33.3[a]
Iodine number (Wijs)	99.92	95.21
Saponification number	194.0	198.00
Ester number	193.9	193.8
Reichert–Meissl number	0.0	0.31
Polenske number	0.0	0.32
Free fatty acids (per cent, oleic)	0.006	0.02
Acetyl number	12.3	12.3
Soluble acids (per cent. as butyric)	0.87[a]	0.56
Insoluble acids (per cent.)	94.16[a]	93.88
Unsaturated acids (per cent.) corrected	73.00	70.10
Saturated acids (per cent.) corrected	20.29	21.36
Iodine number of unsaturated acids	129.18	127.92
Saponification no. of unsaturated acids	199.6	201.2
Unsaponifiable matter	0.64	0.68

[a] Grateful acknowledgment is made to C. A. Tarnutzer and W. W. F. Enz who determined the titer test of the residual oil and the soluble and the insoluble acids of the expressed oils, respectively.

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[3] The average of five determinations of the (ethyl) ether extract of these meats was 68.67%.

nized procedures.[4] Separation of the saturated from the unsaturated acids was effected by the lead salt–ether method[5] after which corrections were made[6] for the small amount of unsaturated acids contaminating them when this procedure is used, and for the unsaponifiable matter accompanying the insoluble acids.

Glycerides of fatty acids of low molecular weight are absent, or at least present in very small amount, a situation pertinent also to sterols and hydroxylated compounds. The low acidity suggests the probable absence of any very active fat splitting enzymes in the nut. Its iodine number assigns this oil to the semi-drying group.

(b) Unsaturated Acids.—Bromination[7] of the unsaturated acids led to the formation of no hexabromide, the derivative of linolenic acid. Appreciable quantities of the tetrabromide (m. p. 114.5°; Br, 53.58%) of linoleic acid were obtained. The bromine content (39.73%) of the dibromide fraction showed that the latter was contaminated with a small amount of the linoleic derivative. Using the former value and the theoretical iodine numbers of oleic and linoleic acids, the percentage composition of the whole was then calculated[8] with the following results.

TABLE II

COMPOSITION OF THE UNSATURATED ACID FRACTION OF THE RESIDUAL OIL

Acid	In oil, %	Glycerides in oil, %	Total,[a] %
Oleic	51.26	53.57	55.64
Linoleic	18.84	19.69	21.65

[a] This column includes the unsaturated acids present with the saturated.

The same acids were qualitatively identified, both by bromine content and melting point, in the unsaturated fraction of the expressed oil.

TABLE III

RESULTS OF ANALYSIS OF METHYL ESTERS OF THE SATURATED FATTY ACIDS

Fraction	Boiling range, 3 mm.	Wt., g.	Iodine no.	Sapon. no.	Mean mol. wt.	Unsatd. acids, g.	Myristic acid, g.	Palmitic acid, g.	Stearic acid, g.
1	145–150	3.52	11.87	213.9	259.34	0.33	1.18	1.84	..
2	150–157	25.56	12.42	208.8	266.20	2.48	3.21	18.60	..
3	157–165	12.51	19.74	205.6	269.35	1.93	0.36	9.63	..
4	165–168	10.58	35.63	197.0	281.55	2.95	..	4.28	2.85
5	168–175	8.28	30.66	193.2	289.62	1.99	..	1.85	4.07
Res.	...	2.30	59.68	167.2	390.50	1.18	..	..	..
	Total	...	...	...	....	..	4.75	36.20	6.92

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[4] Association of Official Agricultural Chemists, "Methods of Analysis," Washington, D. C., 1925, 2d ed., pp. 281–285.

[5] Gusserow, *Arch. Apoth.-Vereins nord Teutschland*, 27, 153 (1828); Varrentrapp, *Ann.*, 25, 197 (1840).

[6] Jamieson, *J. Assoc. Official Agri. Chem.*, 11, 303 (1928).

[7] Eibener and Muggenthaler, *Favben-Ztg.*, 18, 131 (1912).

[8] Baughman and Jamieson, THIS JOURNAL, 42, 157 (1920).

(c) Saturated Acids.—Separation of the methyl esters[8] of the saturated acids into five fractions whose boiling range was 145 to 175° (3 mm.) (Table III) was followed by the calculation of the mean molecular weight of each from saponification and iodine numbers, the latter serving as a measure of the degree of contamination by unsaturated acids. These values lay between 259.3 and 289.6, indicating the presence of esters in the C_{12} to C_{18} group. Myristic, palmitic and stearic acids were subsequently identified by their melting points.

These data lead to the following statement of the percentage composition of the saturated acid fraction.

TABLE IV

COMPOSITION OF THE SATURATED FRACTION OF THE RESIDUAL OIL

Acid	%	Percentage in oil	Glycerides in oil
Myristic	7.94	1.70	1.79
Palmitic	60.48	12.92	13.55
Stearic	11.57	2.47	2.58

The same fatty acids were qualitatively identified by means of their melting points in the corresponding fraction of the expressed oil.

Summary

The chemical and physical characteristics of the expressed and the residual portions of a specimen of Brazil nut oil have been determined. The statement[1] that this oil contains stearin, palmitin and olein has been confirmed. To this list have been added myristin and linolein.

The percentage composition of the residual oil was found to be as follows: myristin, 1.79; palmitin, 13.55; stearin, 2.58; olein, 55.64; linolein, 21.65; unsaponifiable matter, 0.68; residues and undetermined, **4.11.**

MADISON, WISCONSIN

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

THE ACIDITY OPTIMUM OF YEAST HEXOSEDIPHOSPHATASE[1]

BY Z. I. KERTESZ

RECEIVED JULY 28, 1930 PUBLISHED OCTOBER 6, 1930

The hexosediphosphoric acid ester and the enzyme which splits it into fructose and phosphoric acid were discovered by Harden and Young. It has been shown that the enzyme is present in practically all kinds of yeast and also in the *Coli* bacteria. It is present in different organs of the animal body, as well as in many higher plants. Although a great many papers have dealt with yeast hexosediphosphatases, we have but very little information concerning its optimum PH.

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[1] The writer's sincere thanks are due to Professor H. v. Euler and to the Stockhoms Hogskola for the opportunity to make this study.

The *PH* optima of the zymase group of enzymes have been determined by various authors. In spite of the fact that it might be expected that the PH optima of these would be in the same acidity range as that of the yeast fermentation as a whole the experiments have not supported this supposition. Thus the optimum of the hexosedehydrogenase was found to be ***PH*** 8.0–8.5.[2]

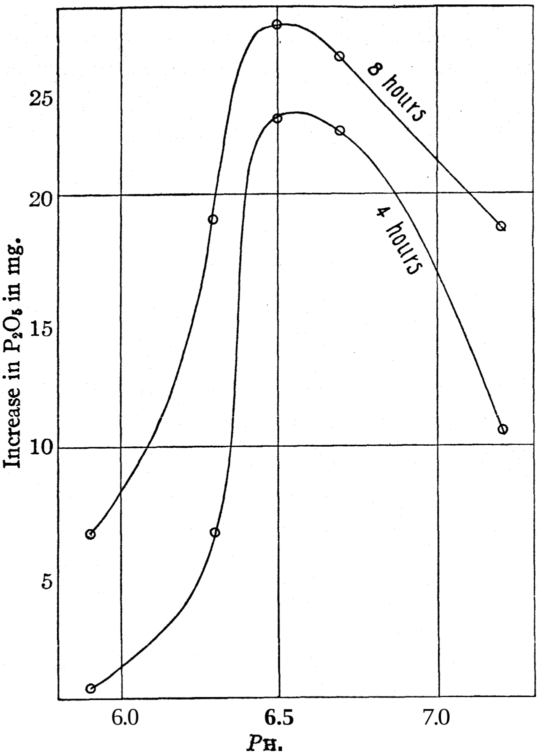

Fig. 1.—The *PH* optimum of hexosediphosphatase.

Euler and Nordlund[3] showed that the optimum of the synthetic enzyme of yeast producing hexosediphosphoric acid ester is at PH 6.4. Because of the obvious importance of knowing this point for all enzymes, it has been determined for yeast hexosediphosphatase.

Experimental

The sodium salt of hexosediphosphate was made from Candiolin by the method of Meyerhof.[4] The yeast applied was a dry preparation of bottom-yeast "H" of the St. Erick Brewery of Stockholm. The zymase of the yeast was very active. The composition of the reaction mixtures was as follows

1.6 g. dry yeast
2.5 cc. 4% hexosediphosphate
2.5 cc. distilled water
5.0 cc. buffer (citric acid, after S. P. L. Sorensen)

The ***PH*** was determined potentiometrically by the use of hydrogen electrodes. The reaction mixtures were kept in a thermostat at 30°. At the beginning and after certain intervals the increase in amount of inorganic phosphoric acid in the reaction mixture was determined by the micro method of Embden.[5]

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[2] **H. v. Euler, K. Myrbäck and R. Nilsson, *Ergeb. der Physiol.*, *26*, *547* (1928).**

[3] **H. v. Euler and F. Nordlund, Z. *physiol. Chem.*, 116, 229 (1921).**

[4] **Meyerhof, *ibid.*, 102, 1 (1918).**

[5] **Embden, *ibid.*, 113, 108 (1921).**

PH OPTIMUM OF YEAST HEXOSEPHOSPHATASE

PH	4 Hours		8 Hours	
	P_2O_5, mg.	Relative action	P_2O_5, mg.	Relative action
5.9	0.4	1.7	6.6	25
6.3	6.6	29	19.0	71
6.5	23.0	100	26.8	100
6.7	22.6	98	25.4	95
7.2	10.6	46	18.8	70

The results are given in the table. In each set the maximum amount of phosphorus pentoxide formed was taken as 100, and the others were calculated as percentages of it. It will be seen that the optimum PH is very close to 6.5. At this *PH* in eight hours about 38% of the substrate was hydrolyzed.

Summary

The *PH* optimum of the yeast hexosediphosphatase has been determined to be *PH* 6.5.

GENEVA, NEW YORK

[CONTRIBUTION FROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS WELLCOME AND COMPANY]

SYNTHESIS OF LODAL AND EPININE

BY JOHANNES S. BUCK

RECEIVED AUGUST 4, 1930 PUBLISHED OCTOBER 6, 1930

Lodal, 4,5-dimethoxy-2-β-methylamino-ethylbenzaldehyde, was obtained by Pyman[1] by the oxidation of laudanosine. It is also related to papaverine, since N-benzoyltetrahydropapaverine can be degraded to 6.7-dimethoxy-3,4-dihydroisoquinoline,[2] whose methochloride (6,7-dimethoxy-2-methyl-3,4-dihydroisoquinolinium chloride) is identical with the compound obtained from lodal by means of hydrochloric acid.

Epinine, 3,4-dihydroxyphenylethylmethylamine, was obtained by Pyman[1,2] by heating 1-keto-6,7-dimethoxy-2-methyltetrahydroisoquinoline, obtained from laudanosine or papaverine, with hydrochloric acid.

Lodal is a post-partum constrictor for uterine vessels, and a styptic in uterine hemorrhage,[3] while epinine shows hemostatic and pressor properties similar to those of adrenaline,[4] with the advantage of greater stability in solution. Up to the present time no complete syntheses of these compounds have been reported. The author has carried out complete syntheses of lodal and epinine, starting from homoveratrylamine (prepared from vanillin). This amine is monomethylated, via the Schiff base, and

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[1] Pyman, J. Chem. Soc., 95, 1266 (1909).

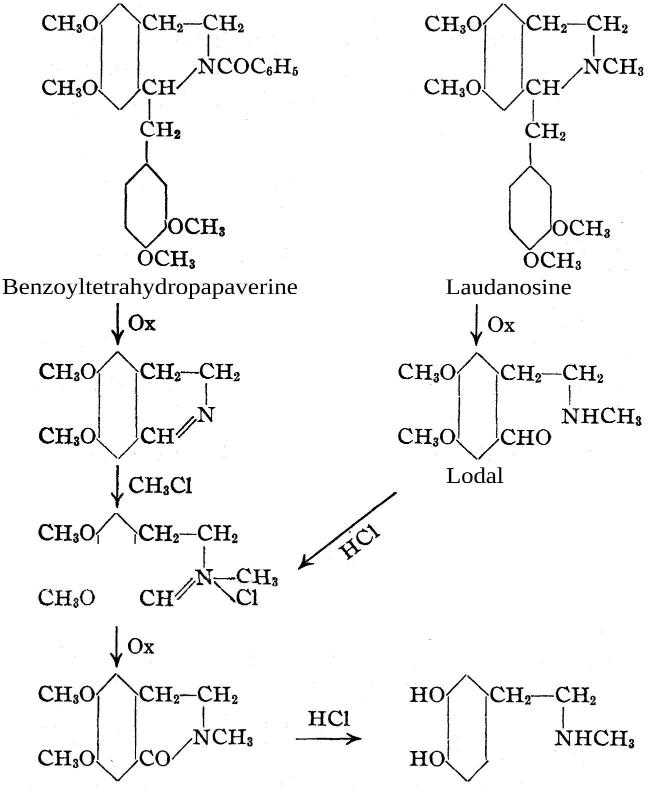
[2] Pyman, *ibid.*, 95, 1610 (1909).

[3] Laidlaw, Biochem. J., 5, 243 (1911).

[4] Barger and Dale, J. *Physiol.*, 41, 19 (1910).

then demethylated to produce epinine hydrochloride. Alternatively, methylhomoveratrylamine is converted into the formyl derivative and this then cyclized by the peculiar reaction of Decker.[5] In both cases the synthetic products were compared with authentic compounds prepared by Pyman's method and found to be identical with these.

The relationships mentioned may be shown thus



Experimental

Homoveratrylamine.[6]—This amine was prepared from dimethoxyphenylpropionamide. Veratric aldehyde was condensed with ethyl acetate and the resulting dimethoxycinnamic ester hydrolyzed and reduced to dimethoxyphenylpropionic acid as described by Perkin and Robinson.[7] By heating the ammonium salt of the acid,[5] dimethoxyphenylpropionamide was obtained. This was then converted into homoveratrylamine by the regular Hofmann method.[5,6]

Methylhomoveratrylamine.—The methylation was carried out by first forming the benzal derivative and then treating this with methyl iodide. The benzal group was then split off, giving methylhomoveratrylamine hydriodide.[5] Molecular amounts of homo-

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[5] Decker, Ann., 395, 390 (1913).

[6] Buck and Perkin, J. Chem. *Soc.*, 125, 1675 (1924).

[7] Perkin and Robinson, *ibid.*, 91, 1080 (1907).

veratrylamine and benzaldehyde were mixed. Heat was evolved and the mixture became turbid through the separation of water, which was then removed by heating under reduced pressure. An equivalent amount of methyl iodide was added and the mixture heated, with the careful exclusion of air and moisture for twenty hours at 37". The resulting solid, yellow, crystalline mass was boiled with 90% alcohol. On cooling and adding ether, the hydriodide of methylhomoveratrylamine separated. The yield was 79% of the theoretical.

The hydriodide after crystallization forms a dull white mass of jagged irregular prisms melting at 131° (uncorr.). It is very soluble in water, readily soluble in alcohol and sparingly soluble in ether.

Anal. Calcd. for $C_{11}H_{18}O_2NI$: C, 40.86; H, 5.57. Found: C, 41.09; H, 5.59.

The base was prepared by adding an excess of strong sodium hydroxide solution to an aqueous solution of the hydriodide and extracting with benzene It forms an almost colorless and odorless oily liquid, b. p. 159° (11 mm.), n_{15} 1.5362; d^{20}_{20} 1.0597. It is very soluble in water, giving an alkaline solution, and is miscible with the usual organic solvents. Unlike homoveratrylamine, it appears not to form a carbonate in air.

Anal. Calcd. for $C_{11}H_{17}O_2N$: C, 67.69; H, 8.72; N, 7.18. Found: C. 68.09; H, 8.65; N, 6.93.

The **picrate,** prepared in aqueous solution, forms a yellow crystalline powder, melting at 162–163" (uncorr.).

Anal. Calcd. for $C_{17}H_{20}O_9N_4$: C, 48.11; H, 4.72. Found: C, 47.95; H, 4.75.

The quaternary iodide, formed when the amine is warmed in alcoholic solution with methyl iodide, consists of beautiful pearly masses of plates. It is soluble in water and alcohol and melts at 226° (uncorr.).

Anal. Calcd. for $C_{13}H_{22}O_2NI$: C. 44.44; H, 6.26. Found: C, 44.37; H, 6.39.

The platinichloride forms a pale orange granular precipitate, melting at 190° (uncorr.) with frothing and blackening.

Anal. Calcd. for $(C_{11}H_{17}O_2N)_2 \cdot H_2PtCl_6$: C, 33.0; H, 4.5; Pt, 24.4. Found: C, 34.0; H, 4.5; Pt, 24.6.

The aurichloride forms a bulky orange powder, melting with frothing and blackening at 148° (uncorr.).

Anal. Calcd. for $C_{11}H_{17}O_2N \cdot HAuCl_4$: C, 24.7; H, 3.4; Au, 36.9. Found: C, 25.0; H, 3.5; Au, 37.4.

Epinine.—Methylhomoveratrylamine hydriodide was heated with five times its weight of hydriodic acid (sp. gr. 1.70) for thirty minutes at 120–130°. Surplus acid was then distilled off under reduced pressure. The residual golden oil was dissolved in water and converted into the hydrochloride by means of silver chloride. The yield of hydrochloride was over 65% of the theoretical. The hydrochloride and the base prepared from it were identical in every respect with authentic specimens prepared by Pyman's method. Mixed melting point determinations showed no depression.

Anal. Calcd. for $C_9H_{14}O_2NCl$: N, 6.88; Cl, 17.42. Found: N, 6.90; Cl, 17.54.

Lodal.—Four and nine-tenths grams of methylhomoveratrylamine and 2.3 g. (2 mols) of absolute formic acid were mixed and the whole heated for one hour in an oil-bath at 210". A clear almost colorless sirup of the formyl compound resulted. This was dissolved in 50 cc. of toluene and boiled with 20 g. of phosphorus pentoxide for thirty minutes. After cooling, the toluene was decanted and the pentoxide added to crushed ice. The solution was then filtered, neutralized with sodium bicarbonate, extracted with benzene, and the aqueous liquor made strongly alkaline with 20% sodium hydroxide solution. On standing, a portion of the product crystallized out and the rest was extracted with benzene; yield, 61% of crude material. The compound was identified by comparison with an authentic specimen and by mixed melting point determinations on the base, the picrate and the very characteristic cyano derivative.

Summary

Complete syntheses of lodal (4,5-dimethoxy-2-β-methylamino-ethylbenzaldehyde) and epinine (3,4-dihydroxyphenylethylmethylamine), from vanillin, via homoveratrylamine, have been carried out. The products were identical with those prepared by Pyman's[1,2] method from papaverine or laudanosine.

Tuckahoe, New York

[Contribution from the Chemical Laboratory of the College of Liberal Arts of Northwestern University]

THE ARSONATION OF AROMATIC ALDEHYDES

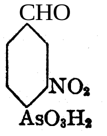
By Albert B. Scott[1] and Cliff S. Hamilton

Received August 4, 1930 Published October 6, 1930

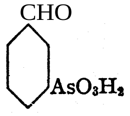
Certain organic arsenical compounds exert a specific curative action in syphilis and the trypanosomiases. Although arsonated aromatic compounds containing the amino group substituted in the nucleus have been widely investigated for many years, little attention has been devoted to arsonated aromatic molecules containing a non-cyclic carbonyl group. The present investigation deals with the preparation and properties of arsonated aromatic aldehydes, molecules which contain a nuclear arsono group (AsO_3H_2) and a non-cyclic carbonyl group. The only reference to this type of substance was found in certain patents. Pfleger and Albert[2] claim derivatives of p-arsonobenzaldehyde. Margulies claims 3-nitro-4-arsonobenzaldehyde and *p*-arsonobenzaldehyde.[3]

Kalberlah[4] claims unique effectiveness for a new aromatic arsenical compound containing a non-cyclic carbonyl group.

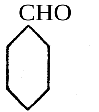
In the present investigation derivatives of three arsonated aromatic aldehydes have been prepared. The structures of the parent compounds are as follows

I


3-Nitro-4-arsono-benzaldehyde

II


m-Arsono-benzaldehyde

III


p-Arsono-benzaldehyde

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[1] Research Fellow under a grant from Parke, Davis & Co. This article is an abstract of a thesis submitted by Albert B. Scott in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Northwestern University.

[2] Pfleger and Albert, United States Patent 1,472,778 (1923).

[3] Margulies, British Patent 220,688 (1924).

[4] Kalberlah, *Klin. Wochschr.*, 48, 2185 (1924).

3-Nitro-4-arsonobenzaldehyde (I) was prepared from 3-nitro-4-aminobenzaldehyde by Bart's reaction.[5] The diazotization proved difficult and was accomplished by the use of a large volume of acetic acid and a great excess of nitrous acid. Arsonation was carried out by adding dilute sodium hydroxide solution to the strongly acid mixture of diazonium compound and arsenious acid. This procedure permits coupling to form the arsonic acid over a wide range of hydrogen-ion concentrations and is consequently advantageous in the preparation of a new arsonic acid where the optimum conditions for coupling are unknown.

Purification of 3-nitro-4-arsonobenzaldehyde was unsatisfactory. The *p*-nitrophenylhydrazone, the β-naphthylhydrazone and the semicarbazone of this arsonated aromatic aldehyde were obtained in pure condition. The method of purification found most suitable for these derivatives was solution in dilute sodium carbonate solution followed by re-precipitation with dilute hydrochloric acid. From the semicarbazone of 3-nitro-4-arsonobenzaldehyde the semicarbazone of 3-amino-4-arsonobenzaldehyde was prepared by reduction with ferrous hydroxide in alkaline medium as suggested by Jacobs, Heidelberger and Rolf[6] and modified by Palmer and Adams.[7] While the alkaline medium was quite satisfactory for the reduction of the semicarbazone it might have been incompatible with the parent aldehyde.

m-Arsonobenzaldehyde was prepared from m-aminobenzaldehyde by Bart's reaction and isolated as the *p*-nitrophenylhydrazone. A solution of m-aminobenzaldehyde was prepared by reduction of *m*-nitrobenzaldehyde as the sodium bisulfite addition compound with ferrous sulfate and calcium carbonate.[8] Excess iron was precipitated from the very dilute solution and the filtrate containing *m*-aminobenzaldehyde was arsonated. m-Aminobenzaldehyde formed tars with remarkable readiness except in neutral or nearly neutral dilute solutions. After arsonation *m*-arsonobenzaldehyde was obtained from the solution as the p-nitrophenylhydrazone.

To avoid the extreme difficulty of working with certain aminoaldehydes, a new and independent method of synthesis of arsonated aromatic aldehydes was developed. *p*-Methylphenylarsonic acid was oxidized to *p*-arsonobenzaldehyde by means of solid chromic oxide (CrO_3) in the presence of acetic anhydride, glacial acetic acid and concentrated sulfuric acid. Formation of the aldehyde diacetate prevents further oxidation of the aldehyde group. The arsonated aromatic aldehyde, *p*-arsonobenzaldehyde, prepared by this method was isolated as the p-nitrophenylhydra-

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[5] Bart, *Ann.*, 429, 55 (1922).

[6] Jacobs, Heidelberger and Rolf, THIS JOURNAL, 40, 1581 (1918).

[7] Palmer and Adams, *ibid.*, 45, 1312 (1923).

[8] German Patent 66,241 (1892).

zone. The yield of *p*-arsonobenzaldehyde was low but the method is being improved and will be extended to other alkyl arsonic acids in the near future. The great advantage of this method of preparing certain arsonated aromatic aldehydes lies in the ease of preparation of the alkyl arsonic acids which serve as intermediates to be oxidized to the corresponding aldehydes.

In this investigation the question of qualitatively proving the presence of the arsono group (AsO_3H_2) arose repeatedly and lack of a suitable qualitative test for arsonation was a marked handicap. Ordinary qualitative tests for arsenic fail completely to differentiate between arsenic in inorganic combination and arsenic in organic combination. The reduction of aromatic arsonic acids to the less soluble arseno compounds by means of hypophosphorous acid was found to be adaptable for use as a rapid qualitative test for the arsonation of aromatic compounds. With all of the arsonic acids examined a characteristic precipitate of the corresponding arseno compound was obtained within twenty minutes under the conditions described in the experimental portion of this work. Experience with this reduction indicates that a mixture of the arsine oxide and arseno compound corresponding to the arsonic acid may form in some cases but this does not affect the validity of the test. However, much more extensive study will be necessary to prove that this qualitative test is general.

Experimental

I. 3-Nitro-4-Arsonobenzaldehyde

3-Nitro-4-aminobenzaldehyde.—Following the method of Hodgson and Beard[9] 3-nitro-4-aminobenzaldehyde was prepared in approximately 10% yield, the greatest loss occurring in the conversion of *p*-nitrotoluene to *p*-acetaminobenzaldehyde. The product after recrystallization from 80% acetic acid melted at 188–189° (Hodgson and Beard give m. p. 191" for the crude product).

Arsonation of 3-Nitro-4-aminobenzaldehyde.—A solution of 16 g. of recrystallized 3-nitro-4-aminobenzaldehyde was obtained by stirring for thirty minutes at 95° with 200 cc. of 80% acetic acid. The hot solution was filtered and then, by cooling to 20°, a thick paste of fine crystals was formed. Diazotization was carried out at 20° with stirring by the simultaneous dropwise addition of 20% sodium nitrite solution and concentrated hydrochloric acid. The dropwise addition was carried out at such a rate that all of the hydrochloric acid (90 cc.) had been added in sixty minutes and all of the sodium nitrite solution (220 cc.) in ninety minutes. After the addition of the sodium nitrite solution was complete, stirring was continued for thirty minutes making a total of one hundred and twenty minutes for the diazotization. The bright red acid diazonium solution was then filtered, treated cautiously with urea, and poured into a 4-liter crock containing 75 cc. of a 20% sodium meta-arsenite solution and 125 cc. of water. Then with constant stirring and below 15° 4 N sodium hydroxide solution was added dropwise until there was 25 cc. excess over the amount necessary to make the solution just alkaline to litmus paper. After standing overnight at room temperature, the dark

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[9] Hodgson and Beard, J. Chem. *Soc.*, 20 (1927).

brown solution was stirred for sixty minutes at 60–70°. At the end of this time a test with alkaline R-salt solution showed that all of the diazo compound had reacted. The solution was then made just acid to litmus paper with hydrochloric acid, heated to boiling with decolorizing charcoal, filtered, made acid to Congo red paper with hydrochloric acid and concentrated to 300 cc. on the steam-bath. The golden yellow solution was then made just neutral to litmus paper with 6 *N* sodium hydroxide solution added slowly with stirring and cooling. The solution of the monosodium salt of 3-nitro-4-arsonobenzaldehyde was then filtered from undissolved material and the free arsonic acid precipitated from the filtrate as a yellow paste by adding 6 N hydrochloric acid drop by drop with stirring and cooling until the solution was acid to Congo red paper. The pasty yellow product was combined with a further quantity recovered from the filtrate and washings and dried in vacuum over calcium chloride to form a heavy yellow amorphous powder which softened and darkened at about 155° and decomposed slowly above this temperature; wt., 12.5 g.; yield, 47%. In one run the arsonic acid was isolated as the semicarbazone and a weight of semicarbazone corresponding to 54% yield of 3-nitro-4-arsonobenzaldehyde was obtained.

The crude arsonic acid gave an arsine odor when burned; gave a precipitate with hypophosphorous acid when warmed in either aqueous or alcoholic solution; dissolved in concentrated ammonium hydroxide, dilute sodium carbonate solution and dilute sodium hydroxide solution; formed a *p*-nitrophenylhydrazone, a β-naphthylhydrazone and a semicarbazone; and was slightly soluble in water while practically insoluble in ethyl alcohol, methyl alcohol, ethyl acetate, ether, chloroform, ligroin and benzene.

Anal. (1) After recrystallization from water. Subs., 0.1448: 21.60 cc. of potassium bromate (1 cc. = 0.001874 g. As). Calcd. for $C_7H_6O_6NAs$: As, 27.25. Found: As, 27.95. (2) After solution in dilute sodium carbonate solution and re-precipitation with dilute hydrochloric acid. Subs., 0.1602: 23.17 cc. of potassium bromate (1 cc. = 0.001874 g. As). Found: As, 27.10.

Analytical values on this substance were not consistent. It was possible, however. to prepare pure derivatives.

***p*-Nitrophenylhydrazone of 3-Nitro-4-arsonobenzaldehyde.—A** clear amber solution of 3.5 g. of crude 3-nitro-4-arsonobenzaldehyde in 400 cc. of water was obtained by boiling, cooling and filtering. To the cooled solution was added 4 g. of solid sodium acetate. The solution was then heated nearly to boiling and a solution of 2 g. of #-nitrophenylhydrazine in 100 cc. of water and 10 cc. of 6 N hydrochloric acid was then poured in with vigorous stirring. A brilliant orange-red flocculent precipitate formed at once. After digestion for ninety minutes this product was filtered, washed with water and ether, and dried in vacuum over phosphorus pentoxide to form an amorphous orange powder which began to decompose at about 260–270°.

The product was purified by dissolving in 10% sodium carbonate solution, filtering and re-precipitating by making just acid to Congo red paper with 6 *N* hydrochloric acid added dropwise with stirring and cooling.[10] After washing and drying as before, an orange amorphous powder was obtained.

Anal. Subs., 0.2484, 0.2759: 23.90, 26.30 cc. of potassium bromate (1 cc. = 0.001874 g. As). Calcd. for $C_{13}H_{11}O_7N_4As$: As, 18.29. Found: As, 18.03, 17.86.

β-Naphthylhydrazone of 3-Nitro-4-arsonobenzaldehyde.—A solution of β-naphthylhydrazine was obtained by dissolving 0.7 g. of β-naphthylhydrazine hydrochloride

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[10] When the sodium carbonate solution of the hydrazone came through the filter with a marked cloudy or silky appearance, it was warmed with a small amount of decolorizing charcoal and filtered again. This treatment gave a solution which was free from suspended fine particles.

in **100 cc.** of boiling water, adding **0.3** g. of solid sodium acetate, cooling to about 50° and filtering. This solution was then poured, with vigorous stirring, into a hot solution of **1** g. of crude 3-nitro-4-arsonobenzaldehyde in **200** cc. of water, and the heavy brick-red precipitate digested, washed and dried. The dry dark red powder darkened at about **210"** and decomposed at about 235–245°; wt., **0.75 g.** For purification **3** g. of the crude hydrazone was treated with **5** cc. of 10% sodium carbonate solution and **200** cc. of water and filtered. The insoluble residue was treated with 5 cc. of 10% sodium carbonate solution and 50 cc. of water and filtered. The combined filtrates were muddy and a clear solution was obtained by warming with decolorizing charcoal and again filtering. From the final clear red solution the hydrazone was precipitated by the addition of **6** N hydrochloric acid added dropwise with stirring and cooling until the solution was acid to Congo red paper.

Anal. Subs., **0.2322, 0.2334: 22.20, 22.40** cc. of potassium bromate (**1** cc. = **0.001874** g. As). Calcd. for $C_{17}H_{14}O_6N_3As$: As, **18.07.** Found: As, **17.92, 17.99.**

The Semicarbazone of **3-Nitro-4-arsonobenzaldehyde.**—A solution of **1** g. of semicarbazide hydrochloride in **50 cc.** of water was added to a clear solution of **2** g. of crude 3-nitro-4-arsonobenzaldehyde in **400** cc. of water containing **0.73** g. of solid sodium acetate. The solution became cloudy and immediately deposited heavy yellow crystals. When dried the semicarbazone was a pale yellow powder which began to darken at about 220° and decomposed at about 250°; wt., **1.62g.**

For purification the semicarbazone was recrystallized twice from methyl alcohol and then **2** g. of the recrystallized material was treated with 10% sodium carbonate until nearly all of it dissolved. The golden yellow solution obtained by filtering was then made just acid to Congo red paper by adding **6** N hydrochloric acid dropwise with stirring and cooling. The light yellow product dried to form an almost white crystalline powder.

Anal. **(1)** Recrystallized twice from methyl alcohol. Subs.. 0.1906, **0.2385:** 22.50, 28.20 cc. of potassium bromate (1 cc. = **0.001874** g. As). Calcd. for $C_8H_9O_6N_4As$: As, **22.59.** Found: As, **22.12, 22.16. (2)** Recrystallized material after solution in dilute sodium carbonate solution and re-precipitation with dilute hydrochloric acid. Subs., **0.2374: 28.40** cc. of potassium bromate (**1** cc. = **0.001874** g. As). Found: As, **22.42.**

The semicarbazone of 3-nitro-4-arsonobenzaldehyde was found to be readily hydrolyzed by heating on the steam-bath with dilute hydrochloric acid.

Semicarbazone of **3-Amino-4-arsonobenzaldehyde.—A** solution of **20** g. of the semicarbazone of 3-nitro-4-arsonobenzaldehyde in **200 cc.** of water and **10** cc. of **6** *N* sodium hydroxide solution was added to a mixture of **127** cc. of **3.3** molar ferrous chloride and **170** cc. of **6** *N* sodium hydroxide solution in a bottle with a wide mouth and the bottle tightly stoppered. The mixture turned reddish-brown at once but was subjected to occasional shaking during sixty minutes and was then filtered through a large Biichner funnel. The filtrate was made just acid to Congo red paper with 3 N hydrochloric acid. The brown pasty precipitate dried to a light brown powder; wt., **11.0** g. The material did not fuse but a gas was evolved over a considerable range of temperature.

The material was found to be moderately soluble in dilute hydrochloric acid and to give a brilliant red product when diazotized and coupled with alkaline R-salt solution.

Anal. Subs., **0.1980, 0.1962: 26.55, 26.40** cc. of potassium bromate (1 cc. = **0.001874** g. As). Calcd. for $C_8H_{11}O_4N_4As$: As, **24.83.** Found: As, 25.13, 25.22.

II. *m*-Arsonobenzaldehyde

Preparation and Arsonation of ***m*-Aminobenzaldehyde.**—To **2000** cc. of water was added **680** g. of ferrous sulfate and **250** g. of calcium carbonate, the latter as a paste with water. This mixture was heated to 85° and during twenty minutes with stirring 500 cc. of an aqueous solution containing 60 g. of m-nitrobenzaldehyde and 40 g. of solid C. P. sodium bisulfite were added. The mixture turned brown and carbon dioxide was evolved After cooling the solution was acidified to Congo red paper and boiled to expel sulfur dioxide. At this point diazotization was unsuccessful because of excess ferrous salts so the solution was diluted to 4 liters, made faintly alkaline to litmus paper with sodium hydroxide solution and filtered. The m-nminobenzaldehyde in the filtrate as a solution was arsonated. The filtrate was made acid to Congo red paper with hydrochloric acid and then 60 cc. excess of concentrated hydrochloric acid was added. At a temperature below 10°, 207 cc of 20% sodium nitrite solution was added dropwise with stirring. The diazonium solution was then poured into 195 cc. of 20% sodium meta-arsenite solution and 6 N sodium hydroxide was added until the solution was just alkaline to litmus paper. Vigorous nitrogen evolution occurred. The solution, after stirring for one hour at 50°, was made just acid to litmus paper, heated to boiling with decolorizing charcoal, filtered and concentrated to 1000 cc.

Isolation of **m-Arsonobenzaldehyde** as the **p-Nitrophenylhydrazone.**—To 300 cc. of the solution of m-arsonobenzaldehyde at 100° was added a solution containing 4 g. of p-nitrophenylhydrazine, 500 cc. of water, 20 cc. of 6 N hydrochloric acid and 8.3 g. of solid sodium acetate. The brilliant orange flocculent precipitate was washed with water and ether and dried in vacuum over phosphorus pentoxide to form an amorphous orange powder which melted with decomposition between 200 and 210°; wt., 5.4 g. The product was purified by three successive re-precipitations with sodium carbonate solution and hydrochloric acid as previously described.

Anal. Subs., 0.1968, 0.1599: 21.60, 17.75 cc. of potassium bromate (1 cc. = 0.001874 g. As). Calcd. for $C_{13}H_{12}O_5N_3As$: As, 20.55. Found: As, 20.57, 20.80.

III. p-Arsonobenzaldehyde

Chromic Acid Oxidation of **p-Methylphenylarsonic** Acid.—The quantities used in this procedure correspond to those recommended by Thiele and Winter[11] for the oxidation of p-nitrotoluene to p-nitrobenzaldehyde. A solution of 15.8 g. of p-methylphenylarsonic acid in 80 g. of acetic anhydride. 80 g. of glacial acetic acid, and 30 g. of concentrated sulfuric acid was treated with 20 g. of solid chromic oxide (CrO_3) added during thirty minutes. The temperature was maintained at 0–lo°. The mixture was stirred for thirty minutes at 10° following the addition of all of the chromic oxide and was then extracted with two 175-cc. portions of ether. The ethereal extract was taken almost to dryness under diminished pressure, diluted with about 50 cc. of water and 6 g. of a gray solid filtered off.

Isolation of p-Arsonobenzaldehyde as the **p-Nitrophenylhydrazone.**—In order to hydrolyze p-arsonobenzal diacetate, 2 g. of this gray solid was heated for thirty minutes on the steam-bath with 10 cc. of 6 N hydrochloric acid. Then 150 cc. of water was added, the solution filtered and treated with p-nitrophenylhydrazine. The flocculent golden-yellow precipitate was digested for sixty minutes on the steam-bath, filtered, washed and dried to a fine yellow powder; wt., 0.44 g.

Anal. Subs., 0.2006, 0.2047: 22.55, 23.00 cc of potassium bromate (1 cc. = 0.001874 g. As). Calcd. for $C_{13}H_{12}O_5N_3As$: As, 20.55. Found: As, 21.07, 21.06.

IV. Rapid Qualitative Proof of Arsonation of Aromatic Compounds

Enough of the compound was placed in a test-tube to cover the bottom, about 3 cc. of water added, the mixture heated to boiling, cooled and filtered. To the perfectly clear aqueous solution was then added 5 cc. of concentrated hypophosphorous acid.

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[11] Thiele and Winter, Ann., 311,353 (1900).

The tube was placed in a water-bath at 100° and observations made every two or three minutes. With every arsonic acid examined a characteristic precipitate of the corresponding arseno compound (with perhaps some arsine oxide) was obtained within twenty minutes. When a solution of arsenic trioxide in dilute hydrochloric acid was treated with hypophosphorous acid under these conditions, no precipitate was obtained. Table I summarizes the results obtained in testing a series of arsonic acids. In two cases it was found more satisfactory to dissolve the arsonic acid in hypophosphorous acid and omit the water.

TABLE I

ACTION OR HYPOPHOSPHOROUS ACID

	Arsonic acid	Solvent	Minutes for reduction	Color of precipitate
1	p-Hydroxyphenylarsonic acid	H_2O	4	Red
2	Phenylarsonic acid	H_2O	1	White
3	Mono-sodium salt of *p*-arsonophenoxyethanol	H_2O	1	Pale yellow
4	p-Arsanilic acid	(a) H_2O	19	Red
		(b) H_3PO_2	13	Solid red mass
5	Tryparsamide		2	Red
6	3-Nitro-4-aminophenylarsonic acid	H_2O	2	Golden-yellow

Summary

1. A rapid qualitative test of arsonation for aromatic compounds has been suggested.

2. A new type of arsonic acid, the arsonated aromatic aldehyde, has been developed.

3. The preparation of three arsonated aromatic aldehydes, 3-nitro-4-arsonobenzaldehyde, m-arsonobenzaldehyde and *p*-arsonobenzaldehyde has been described *p*-Arsonobenzaldehyde was prepared by a new and independent synthetic method.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE REACTION BETWEEN HIGHLY PHENYLATED COMPOUNDS AND ORGANIC MAGNESIUM COMPOUNDS

BY E. P. KOHLER AND E. M. NYGAARD

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A study of the reaction between α,β-unsaturated ketones and organic magnesium compounds, made many years ago, included every member except the last of a series beginning with acrolein and ending with its most highly phenylated substitution product, tetraphenyl propenone. In view of the increasing interest in highly phenylated compounds and especially of our own results with highly phenylated unsaturated nitro compounds, it was desirable to complete the study of this series.

We have, therefore, investigated the behavior of the completely phenylated unsaturated ketone I both toward methyl magnesium iodide and toward phenyl magnesium bromide. And since the results were rather surprising, we also included in the investigation the behavior of the corresponding saturated ketone, α,β,β-triphenylpropiophenone, II.

$$\underset{\text{I}}{(C_6H_5)_2C{=}C(C_6H_5)COC_6H_5} \qquad \underset{\text{II}}{(C_6H_5)_2CHCH(C_6H_5)COC_6H_5}$$

We found that the saturated ketone reacts much more readily than we had anticipated, both with methyl magnesium iodide and with phenyl magnesium bromide. Indeed the reaction with methyl magnesium iodide proceeds rapidly in ethereal solution at the ordinary temperature, and the yield of the tertiary alcohol to be expected is practically quantitative. The structure of the product was established by treating it with a dehydrating agent and ozonizing the resultant hydrocarbon. The oxidation product was the original ketone

$$\underset{\text{II}}{(C_6H_5)_2CHCH(C_6H_5)COC_6H_5} \longrightarrow \underset{\text{III}}{(C_6H_5)_2CHCH(C_6H_5)C(CH_3)(C_6H_5)OH} \longrightarrow$$

$$(C_6H_5)_2CHCH(C_6H_5)C(C_6H_5){=}CH_2 \longrightarrow \underset{\text{IV}}{(C_6H_5)_2CHCH(C_6H_5)COC_6H_5}$$

With phenyl magnesium bromide the saturated ketone reacts less readily, but this reaction can likewise be completed in ether, at the ordinary temperature. In this case also the principal product is the tertiary alcohol but the yield is not nearly so good, doubtless because of the ease with which the highly phenylated carbinols undergo cleavage to a mixture of simpler products. The proof of the structure of the Grignard product was obtained by oxidation. The carbinol was readily oxidized by chromic acid in glacial acetic acid, and yielded two moles of benzophenone to one of benzoic acid.

$$\text{II} \longrightarrow \underset{\text{V}}{(C_6H_5)_2CHCH(C_6H_5)C(C_6H_5)_2OH} \longrightarrow 2(C_6H_5)_2CO + C_6H_5CO_2H$$

In sharp contrast with the saturated ketone, the corresponding unsaturated compound does not react at all with either of the Grignard reagents at the ordinary temperature, and it was recovered even after prolonged boiling. In order to secure any reaction it was necessary to replace most of the ether with benzene and operate at a higher temperature.

The reaction between the unsaturated ketone and methyl magnesium iodide gave two solid products and a small quantity of oil. The composition of the principal product indicates that it is formed as a result of the addition of one molecule of methyl magnesium iodide to the unsaturated ketone. The second product, always formed only in relatively small quantities, is a hydrocarbon which is doubtless formed from the primary product by loss of water.

A quantitative examination of the behavior of the primary product toward methyl magnesium iodide showed that it reacts with only one mole of the reagent and liberates one mole of gas; it therefore probably is a hydroxyl compound. It reacts with ozone and is in part converted into a peroxide, and in part oxidized to benzophenone and other products. These transformations indicate that the substance is a tertiary alcohol formed by addition to the carbonyl group. The results are, however, not quite conclusive because it was impossible to prove the presence of methyl benzoin in the ozonization products.

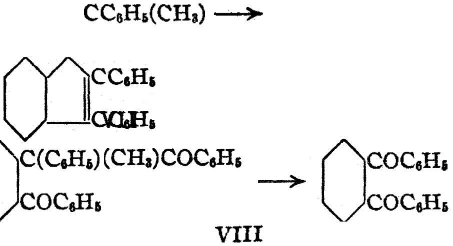
$$\underset{\text{I}}{(C_6H_5)_2C{=}C(C_6H_5)COC_6H_5} \longrightarrow \underset{\text{VI}}{(C_6H_5)_2C{=}C(C_6H_5)C(C_6H_5)(CH_3)OH} \longrightarrow$$

$$(C_6H_5)_2CO + C_6H_5COC(C_6H_5)(CH_3)OH$$

More definite proof of the structure of the substance was obtained by studying the hydrocarbon that is formed in the same reaction. This hydrocarbon can be obtained at will by heating the primary product with acetic anhydride and sodium acetate. When it is gently oxidized with chromic acid, it first combines with two atoms of oxygen and forms a diketone and when this diketone is oxidized more intensively it passes into ortho dibenzoyl benzene. The hydrocarbon is, therefore, methyl triphenyl indene and the primary product must be the carbinol, VI.

$$(C_6H_5)_2C{=}C(C_6H_5)C(CH_3)(C_6H_5)OH \longrightarrow$$

VI



VIII

It proved to be far more difficult to establish the course of the reaction with phenyl magnesium bromide because, although the conditions under which the experiments were conducted were varied in every conceivable manner, the almost invariable result was a mixture of heavy oils from which but little solid product could be extracted. It was not until we adopted the device of decomposing the magnesium compound with acid at the lowest possible temperature and subjecting the product to the action of air or oxygen that we began to get solids in sufficient quantity for examination.

It is known from earlier experiments,[1] that when the enolic modifications which are obtained by 1,4-addition to such unsaturated ketones as contain a hydrocarbon residue in the a-position are exposed to oxygen they form peroxides. This procedure in our case likewise resulted in the addition of a molecule of oxygen but surprisingly enough the product had a deep yellow color. We were therefore confronted with the fact that we had started with a colorless unsaturated compound, added first the equivalent of a

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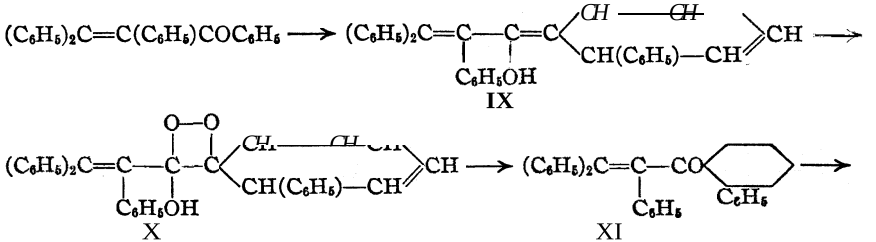
[1] Kohler, *Am. Chem. J.*, 36, 181 (1908).

molecule of benzene and then a molecule of oxygen, and had ended with a deep yellow product which to all appearances was more highly unsaturated than our original substance. The conclusion appeared inevitable that a benzene ring had become involved in the reaction. The transformations of the product confirmed this conclusion.

When the yellow peroxide was treated with cold sodium methylate, which usually cleaves these enolic peroxides, it lost oxygen and water and passed into a new yellow compound which had the composition $C_{33}H_{24}O$. This new yellow compound was subjected to the action of ozone, which, as usual, added two atoms of oxygen and gave two products—benzophenone and a third yellow substance with the composition $C_{20}H_{14}O_2$.

Inasmuch as a yellow compound that is formed by ozonization is most likely to be an a-diketone, we treated this yellow ozonization product with ortho phenylene diamine and found that it readily formed a glyoxaline derivative. Ortho diketones are most cleanly oxidized with alkaline hydrogen peroxide, which cleaves them between the two carbonyl groups. With this reagent our third yellow product gave, quantitatively, benzoic and ortho phenyl benzoic acids.

The organic degradation products of our peroxide are, therefore, benzophenone, benzoic acid and ortho phenyl benzoic acid. The ortho phenyl benzoic acid proves that one of the phenyl groups participates in the reaction, and when all the degradation products are reassembled in their proper order they show quite conclusively which of the phenyl groups is involved, the long series of transformations being represented as follows



IX

X

XI

$$(C_6H_5)_2CO + C_6H_5COCOC_6H_4C_6H_5\ (o) \longrightarrow C_6H_5CO_2H + C_6H_5C_6H_4CO_2H\ (o)$$

XII

In addition to the 1,4-addition product IX, there is formed a relatively small quantity of an unstable colorless compound. This substance liberates gas from methyl magnesium iodide and is capable of forming an acetate. Since it is colorless it cannot be the enol IX, but it might be either a rearrangement product of the enol (XIV) or the 1,2-addition product (XV)

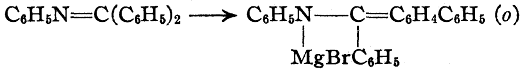
$$(C_6H_5)_2C{=}C(C_6H_5)CHOHC_6H_4C_6H_5\ (o) \qquad (C_6H_5)_2C{=}C(C_6H_5)C(C_6H_5)_2OH$$

XIV XV

In order to distinguish between these two possible formulas we oxidized the acetate and found that one mole of the substance gives one mole of benzoic acid and two moles of benzophenone, proving that the substance must be the 1,2-addition product. Our total yield of definite products is unsatisfactory; at best, we account for only 70% of the unsaturated ketone. But whether this low yield is due to the formation of other substances or the difficulty of isolating these unstable compounds we have been unable to ascertain.

Taken in their entirety, our results show that the most highly phenylated α,β-unsaturated ketone, like most other members of the series, is capable of forming both 1,2- and 1,4-addition products with organic magnesium compounds. Here, however, the resemblance ceases. In all other cases in which both types of addition occur, the relative quantity of the 1,4-addition product is always larger with alkyl than with aryl magnesium compounds. In our case these relations are completely reversed. Methyl magnesium bromide gives no 1,4-addition product, phenyl magnesium bromide but little of the 1,2-product.

A much more interesting difference, however, is represented by the fact that it is not, as in the case of all other members of this series, the ethylenic system but a phenyl group that is involved in 1,4-addition. The first—and only other—case of an addition of this type was reported last year. The two cases are not dissimilar. Gilman and his co-workers[2] found that benzophenone anil reacts with phenyl magnesium bromide only at a relatively high temperature, and that the reaction then consists in 1,4-addition and involves one of the phenyl groups



$$C_6H_5N{=}C(C_6H_5)_2 \longrightarrow C_6H_5\underset{\textstyle MgBr}{N}{-\!-}\underset{\textstyle C_6H_5}{C}{=}C_6H_4C_6H_5\ (o)$$

These two cases serve to diminish to some extent the difference between aromatic and ethylenic systems. It is clear that a phenyl group will participate in a reaction involving 1,4-addition when the hindrance to every other reaction is sufficiently great. It is far from clear, however, why there should be so much more hindrance to 1,2-addition in the unsaturated than in the saturated ketone.

Experimental Part

I. Preparation of Materials

No better methods were found for preparing either the saturated or the unsaturated ketones, but the yields have been improved greatly by modifying the procedure at nearly every stage. The steps involved in the preparation of the saturated ketone are shown in the following series of formulas

$$C_6H_5CHOHCOC_6H_5 \longrightarrow C_6H_5CH_2COC_6H_5 \longrightarrow C_6H_5CHClCH(C_6H_5)COC_6H_5 \longrightarrow$$
$$C_6H_5CH{=}C(C_6H_5)COC_6H_5 \longrightarrow (C_6H_5)_2CHCH(C_6H_5)COC_6H_5$$

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[2] Gilman, Kirby and Kinney, THIS JOURNAL, 51, 2252 (1929).

For the reduction of benzoin to desoxybenzoin we used zinc and glacial acetic acid as recommended by Sudborough,[3] but by introducing an effective mechanical stirrer and by raising the temperature from that of the steam-bath to that of the boiling point of the liquid we not only greatly decreased the time of heating but improved the yield as well. The success of this method depends almost entirely on the quality of the zinc dust. With the finely powdered zinc which is frequently sold as zinc dust the yield is small. Instead of separating a part of the product by crystallization we found it advantageous to subject the entire product to distillation under diminished pressure.

Desoxybenzoin.—Two lots. each of 346 g. of benzoin, 600 g. of glacial acetic acid and 105 g. of zinc dust contained in a flask provided with a mechanical stirrer and an air condenser, were heated in an oil-bath at the boiling point of the liquid until a sample no longer gave a flocculent precipitate when it was dropped into water (four to five hours). The benzoin was first dissolved in the acid heated to about 115°, then the zinc dust was added as rapidly as possible without causing frothing, and finally the temperature was raised to the boiling point.

The solution was poured into hot water, the mixture boiled until the oil collected on the bottom, then cooled and filtered. The solid was washed with water and dissolved in alcohol. After removal of the zinc, the alcoholic solution was distilled under ordinary pressure until free from alcohol, then fractionated under diminished pressure. The yield was 534 g. of desoxybenzoin, equal to 82%.

β-Chloro Benzyl Desoxybenzoin.—The desoxybenzoin obtained in the preceding experiment was dissolved in 350 g. of benzaldehyde, the solution cooled in a freezing mixture, and saturated with hydrogen chloride which was passed into it for seven to eight hours. After standing overnight the resulting solid cake was broken up under alcohol, washed—first with alcohol, then with ether—and dried. The yield was 622 g. of chloro compound from 534 g. of desoxybenzoin, equal to 71%.

Benzal Desoxybenzoin.—A suspension of 250 g. of *p*-chloro benzyl desoxybenzoin, 200 g. of fused potassium acetate and 65 g. of dry sodium carbonate in one liter of methyl alcohol was boiled with constant vigorous mechanical stirring for three hours, then cooled and filtered. The solid was washed with sufficient water to remove inorganic salts completely. Its melting point was 100°, only 1° below that of the pure substance, which was obtained by one crystallization from ether. The yield is 180 g.—equivalent to 81%.

The Saturated Ketone (II).—To a solution of phenyl magnesium bromide prepared from 10 g. of magnesium, 50 g. of finely ground benzal desoxybenzoin was added as fast as it dissolved. The mixture was heated for a short time, then cooled and decomposed with ammonium chloride and ammonia in the usual manner. It yielded 61 g. of pure ketone equivalent to 95.8%.

The saturated ketone cannot be brominated. The route to the unsaturated ketone. therefore, follows the course

$$C_6H_5CH{=}C(C_6H_5)COC_6H_5 \longrightarrow (C_6H_5)_2CHC(C_6H_5){=}C(OMgBr)C_6H_5 \longrightarrow$$
$$(C_6H_5)_2CHC(C_6H_5)BrCOC_6H_5 \longrightarrow (C_6H_5)_2C{=}C(C_6H_5)COC_6H_5$$

For the purpose of preparing the α-bromo compound, 100 g. of finely ground benzal desoxybenzoin was added to a solution of phenyl magnesium bromide made from 20 g. of magnesium. The mixture was heated for a short time, then cooled in a freezing mix-

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[3] Sudborough, *J. Cham. Soc.*, **71, 219 (1897).**

ture. To it was added, with constant stirring and very slowly, to avoid local rise in temperature, **120** g. of bromine which had been dried over phosphorus pentoxide. The mixture was poured into ice and hydrochloric acid and shaken until solid began to separate. The ethereal layer was then diluted with petroleum ether. The resulting solid was washed with water, a mixture of ether and petroleum ether and finally petroleum ether alone. The yield of a-bromo compound was **133** g., equivalent to **87%.**

The Unsaturated Ketone.—A suspension of **130** g. of the **α-bromo** compound and an **equal** weight of potassium acetate in **650 g.** of dry ethyl alcohol was boiled for two hours with sufficiently rapid stirring to prevent bumping. Most of the unsaturated ketone separates on cooling, mixed with potassium chloride. After washing and drying it is sufficiently pure for most purposes. The remainder of the product is obtained by distilling off most of the alcohol, diluting the residue with water and extracting with ether. This is less pure and needs to be recrystallized from chloroform and alcohol. The yield was **94.5** g., equal to **89%.**

II. Experiments with the Saturated Ketone

2,3,4,4,-Tetraphenyl Butanol-2 **(III).—Fifteen** grams of the finely ground saturated ketone was added to a solution of phenyl magnesium bromide made from 4 g. of magnesium. There was no perceptible warming and no change in color but the solid gradually dissolved. After remaining for two hours at the ordinary temperature, the clear solution was decomposed with iced ammonium chloride in the usual manner. The washed and dried ethereal layer, on evaporation, left a solid. This was recrystallized from methyl alcohol. The yield was **12.5** g. of pure product and **2** g. of material, largely composed of the same substance as the principal product.

Anal. **Calcd.** for $C_{28}H_{26}O$: **C, 88.8; H, 6.9.** Found: **88.4;** H, 7.0.

The **carbinol** is readily soluble in all common organic solvents except petroleum ether. It **crystallizes** in long, flat needles and melts at **140°.** It appears to be stable in the air but its melting point gradually drops when it is kept over sulfuric acid in a vacuum desiccator.

2,3,4,4-Tetraphenyl Butene **(IV).—A** solution of one gram of the hydroxyl compound in the requisite quantity of glacial acetic acid containing two drops of sulfuric acid was set aside for twelve hours. It deposited **0.71** g. of a colorless solid and when the acid was pumped off it left **0.2** g. more of the same substance. The substance is quite readily soluble in **all** common organic solvents including petroleum ether. It was recrystallized from methyl alcohol, from which it separated in needles melting at **104–106".**

Anal. **Calcd. for $C_{28}H_{24}$: C, 93.3; H, 6.7.** Found: **C, 93.2; H, 6.9.**

Ozonization.—A current of ozonized oxygen containing about **6%** of ozone was passed through a solution of **2** g. of the hydrocarbon in ethyl bromide for two hours. A considerable quantity of a crystalline solid separated from the solution during the passage of the ozone and more of the same substance was obtained when the ozonized solution was manipulated in the usual manner. The solid had the melting point of the saturated **ketone—tetraphenyl** propanone—and it caused no depression of the melting point when it was mixed with this ketone. The saturated ketone was **likewise** obtained when the hydrocarbon was oxidized with permanganate.

1,1,2,3,3-Pentaphenyl Propanol-1 (V).—A solution of 5 g. of the saturated ketone in dry benzene was added to a solution of phenyl magnesium bromide which had been made from 1.4 g. of magnesium and cooled in a freezing mixture. After the addition, the solution was stirred at the ordinary temperature for an hour. A test made at this time still showed much unchanged ketone. The mixture was therefore set aside for seven hours, then decomposed with iced acid in the usual manner. In addition to much oil, it gave **3.0** g. of a solid melting at **158–159°—a** yield of about **33%.**

All attempts to reduce the quantity of oil and increase the yield of the solid carbinol were unsuccessful. Lowering *the* temperature and stopping the reaction sooner resulted in mixtures of products and unchanged substance which were difficult to handle, and decomposing with ice and ammonium chloride in place of hydrochloric acid had no effect on the yield.

The solid product was purified by crystallizing it from methyl alcohol, from which it separates in the form of small white prisms melting at 159°.

Anal. Calcd. for $C_{33}H_{28}O$: C, 90.0, H, 6.4. Found: C, 89.5; H, 6.8.

A test by the Zeisel method showed that the substance has no alkoxyl group, and a quantitative examination of its reaction with a solution of methyl magnesium iodide in iso-amyl ether showed that it reacts with one mole of the reagent and liberates one mole of gas.

Oxidation.—All attempts to eliminate water from the hydroxyl compound led to unmanageable oils. The compound was therefore oxidized with excess of chromic acid in hot glacial acetic acid. To this end one gram of the substance in glacial acetic acid was treated with excess of chromic acid and heated on a steam-bath for two hours. It yielded 0.73 g of benzophenone and 0.16 g. of benzoic acid, instead of 0.83 g. of the former, 0 2 g. of the latter assuming that one mole of substance gives two moles of the ketone and one mole of the acid.

III. Experiments with the Unsaturated Ketone

A. Reaction with Methyl Magnesium Iodide

The reaction between methyl magnesium iodide and the unsaturated ketone was carried out a great many times. In the early experiments we became convinced that the reaction would not run in ether alone, no matter how prolonged the boiling. We then turned to benzene and found that the minimum temperature at which the reaction would run at an appreciable rate was about 50".

In subsequent experiments, therefore, we used four equivalents of the reagent. replaced the ether with benzene, heated for periods ranging between forty minutes and ten hours and decomposed sometimes with ice and acid, sometimes with ice and ammonium chloride. The yields of carbinol varied from 53.6 to 63.4%. In addition to the carbinol the product usually contained small quantities of its dehydration product—methyl triphenyl indene. No evidence was found for any 1.4-addition product. The lack of color showed conclusively that no phenyl group was involved in the reaction, and the inability to obtain a peroxide was good even if inconclusive evidence that no other type of 1,4-addition had occurred.

2,3,4,4-Tetraphenyl Butenol-2 (VI).—A solution of 10 g. of the unsaturated ketone in 60 cc. of dry benzene was added rapidly to a solution of methyl magnesium iodide which had been prepared in an atmosphere of dry nitrogen from 2.72 g. of magnesium. The mixture was heated to 60° for ten hours while a current of dry nitrogen was passed through the apparatus. After decomposing the magnesium compounds with ice and ammonium chloride in the usual manner, the benzene-ether layer was washed, dried and evaporated in a current of dry air. It deposited a solid which after washing with petroleum ether melted at 96.5°, therefore was pure carbinol. The petroleum ether washings yielded 0.8 g. of methyl triphenyl indene. The rest was oil.

The carbinol dissolves freely in all common organic solvents except petroleum ether. It crystallizes well From ether and petroleum ether and it can also be recrystallized from methyl alcohol and water. It separated in white plates and melts at 96.5'.

Anal. Calcd. for $C_{28}H_{24}O$: C, 89.4; H, 6.4. Found: C, 89.5; H, 6.7.

Proof of Hydroxyl Group.—One mole of the substance reacted with one mole of methyl magnesium iodide and liberated one mole of methane.

Proof of Double Linkage.—The carbinol was ozonized in ethyl bromide with ozonized oxygen containing 6% ozone. The product, decomposed with ice in the usual manner, and then set aside, slowly deposited a small quantity of solid. After recrystallization from alcohol the solid melted with decomposition at about 148°. Its composition corresponds to that of a peroxide of the carbinol and it flashed when it was heated rapidly.

Anal. Calcd. for $C_{28}H_{24}O{\cdot}O_2$: C, 82.4; H, 5.9. Found: C, 82.3; H, 6.0.

The oil that was left after the removal of the peroxide was distilled with steam. The oil in the distillate formed an oxime which melted at 141° and a phenylhydrazone melting at 138°, therefore was benzophenone.

Conversion into Methyl Triphenyl Indene.—A solution of one gram of the carbinol and the same quantity of sodium acetate in acetic anhydride was boiled for five hours, then poured into water and made alkaline with excess of sodium carbonate. The alkaline solution was extracted with ether, the ethereal layer washed, dried and evaporated. It left a solid which after washing with a little ether proved to be pure methyl triphenyl indene. The yield was 0.67 g.

Methyl Triphenyl Indene (VII).—The indene derivative, as has been shown, can be obtained in an excellent yield by heating the carbinol with a suitable condensing agent. It was generally obtained in small quantities as a by-product of the Grignard reaction. In one experiment, 50 g. of the ketone gave 12 g. of the pure indene derivative. Whether this uncommonly large yield was formed during the reaction or during the decomposition of the magnesium derivatives with hydrochloric acid could not be ascertained because we were unable to duplicate the result. The indene crystallizes from absolute ethyl alcohol in the form of prisms melting at 118°.

Anal. Calcd. for $C_{28}H_{22}$: C, 93.9; H, 6 2; mol. wt., 358. Found: C, 93.8; H, 6.2; mol. wt., 320.

Oxidation: α,α,α-Benzoyl-methyl-phenyl-ortho-tolyl Phenyl Ketone (VIII).—A solution of 1.5 g. of the hydrocarbon and 1.2 g. of chromic acid in glacial acetic acid was warmed until oxidation began at 50–60°. The temperature was held at this point for fifteen minutes. The solution was then diluted with water and extracted with ether. The washed and dried ethereal solution was concentrated and diluted with petroleum ether, whereupon it deposited a solid. The solid was recrystallized from anhydrous ether, from which it separated in white prisms melting at 182°.

Anal. Calcd. for $C_{28}H_{22}O_2$: C, 86.2; H, 5.6. Found: C, 86.4; H, 5.2.

Ortho Dibenzoyl Benzene.—The oily mother liquors from the diketone were oxidized with a larger quantity of chromic acid. The principal product was o-dibenzoyl benzene, which was identified by comparison with a sample on hand. Ortho dibenzoyl benzene was also one of the products formed when the oily by-products of the Grignard reaction were oxidized with excess of chromic acid.

B. Reaction with Phenyl Magnesium Bromide

A series of preliminary experiments showed that the unsaturated ketone does not react with phenyl magnesium bromide in boiling ether and that when the reaction was carried out in boiling benzene no solid products could be isolated. We used, therefore, a large excess of the reagent—usually four equivalents—and operated at temperatures between 45–60°. The procedure most favorable for securing the peroxide was the least favorable for isolating the unstable 1,2-addition product. Moreover, the acetate of the 1,2-addition product was most easily obtained directly from the magnesium derivative

$$(C_6H_5)_2C{=}C(C_6H_5)COC_6H_5 \longrightarrow (C_6H_5)_2C{=}C(C_6H_5)C(C_6H_5)_2OMgBr \longrightarrow$$
$$(C_6H_5)_2C{=}C(C_6H_5)C(C_6H_5)_2OCOCH_3$$

The Peroxide (X).—A solution of 15 g. of the ketone in 90 cc. of benzene was added drop by drop to an ethereal solution of phenyl magnesium bromide that was made from 4.08 g. of magnesium. Each drop of the solution produced a momentary red color, which turned to yellow, but by the time all of the ketone had been added, the color of the solution was dark red to brown. Ether was boiled off until the boiling point of the solution reached 50–52°.

After the solution had been boiled at 50–52° for an hour, it was cooled and poured into iced hydrochloric acid contained in a separating funnel. The mixture was shaken vigorously, the acid layer drawn off and the ethereal layer rapidly washed with ice water. The washed ethereal solution was then transferred to a suction flask which was cooled with ice while a rapid current of air was drawn through it. A yellow precipitate soon began to separate. This was collected on a filter when the solution became too thick; a second crop was obtained by diluting the oily residue with ether and repeating the operation, and a third by treating the oil with ether and petroleum ether. The total yield was 7.3 g., equivalent to 37.3%.

The peroxide was recrystallized from ether, from methyl alcohol, and from chloroform, but it is doubtful that this increased its purity. Its melting point varied with the mode of heating, the highest being 186.5".

Anal. Calcd. for $C_{33}H_{26}O_3$: C, 84.3; H, 5.5. Found: C, 84.0; H, 6.0.

In the machine one mole of the compound consumed three moles of methyl magnesium iodide and liberated one mole of gas. The peroxide crystallizes in long yellow prisms.

Ozonization.—The peroxide was oxidized with ozone in the usual manner but the results were not very instructive. It gave a considerable quantity of benzophenone, showing that the ethylene linkage was intact but, as was to be expected, the remainder of the molecule was converted into highly colored oils from which only benzoic acid could be isolated.

Reaction with Sodium Methylate. The Unsaturated Ketone (XI).—When the peroxide is added to a concentrated solution of sodium methylate in methyl alcohol it dissolves in part and forms a brilliant red solution, but the ketone begins to separate before solution is complete. The reaction appears to be complete in an hour, but the mixture was usually set aside overnight. Thus 2.5 g. of the finely ground peroxide was added to 20 cc. of 10% sodium methylate. The mixture was set aside for fifteen hours, then diluted with water and extracted with ether. The washed and dried yellow ethereal solution, on evaporation, deposited 2.45 g. of crude product. This was washed with methyl alcohol and further purified by recrystallization from the same medium. The yield of pure ketone was 1.6 g., equivalent to 69%.

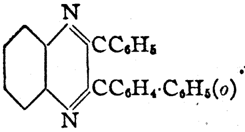
Anal. Calcd. for $C_{33}H_{24}O$: C, 90.8; H, 5.5; mol. wt., 436. Found: C, 90.9; H, 5.6; mol. wt., 412.

The color of the ketone is a lighter yellow than that of the peroxide. It crystallizes in long plates and melts at 138°.

Ozonization: Ortho Phenyl Benzil (XII).—A current of ozonized oxygen containing about 6% of ozone was passed through a solution of one gram of the ketone in ethyl bromide for one and one-half hours The ozonide was decomposed in the usual manner and the solvent removed. The residue was an oil which partially solidified when it was rubbed with alcohol. The resulting solid was recrystallized from alcohol, from which it separated in pale yellow plates melting at 80".

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.9; H, 4.9. Found: C, 83.5; H, 5.3.

The filtrate from the diketone was distilled with steam and the distillate extracted with ether. The ethereal solution contained benzophenone, which was identified by converting it into phenylhydrazone and comparing this with a sample on hand.

The Glyoxaline Derivative, 
.—An alcoholic solution of 0.1 g. of the diketone, 0.09 g. of ortho phenylene diamine hydrochloride and an equivalent quantity of sodium acetate was boiled for a short time, then diluted with water and extracted with ether. The ethereal extract was freed from excess of the diamine by shaking with dilute acid, then washed, dried and evaporated. It deposited a colorless solid. The solid was recrystallized from alcohol, which deposited it in large square plates which melted at 163°.

Anal. Calcd. for $C_{26}H_{18}N_2$: C, 87.1; H, 5.0. Found: C, 86.6; H, 5.1.

Oxidation of the Diketone: Ortho Phenyl Benzoic Acid.—A solution of 0.2 g. of the diketone in methyl alcohol was treated first with excess of 15% hydrogen peroxide, then with excess of 10% sodium hydroxide. It soon became colorless. It was then heated to remove the methyl alcohol, and acidified. From the acid solution ether extracted 0.23 g. of a mixture of acids which could not be separated by steam distillation. but which was readily separated by sublimation. The sublimate was benzoic acid. The residue (0.15 g.) melted at 113°. It was identified as ortho phenyl benzoic acid by comparison with a sample of this acid which was obtained by fusing fluorenone with potassium hydroxide.

Triphenylvinyl Diphenyl Carbinol (XV).—A solution of 10 g. of the ketone was added in the usual manner to a solution of phenyl magnesium bromide made from 2 7 g. of magnesium. The mixture was heated to 60° for two hours, then decomposed with iced hydrochloric acid. The ethereal layer was washed, dried and then evaporated in *a* draught. It first deposited the yellow peroxide, and later a colorless solid which was purified by recrystallization from ether–petroleum ether; yield, 12%.

Anal. Calcd. for $C_{33}H_{26}O$: C, 90.4; H, 5.9. Found: C, 90.1; H. 6.0.

The carbinol is sparingly soluble in alcohol, moderately soluble in ether. It crystallizes in thin white plates. It melts with decomposition, and the melting point varies with the rate of heating. The highest melting point observed was 169°. Even the purest samples slowly change at the ordinary temperature, turning ultimately into brown viscous oils, but it can be kept apparently without change at 0°.

The Acetate (XVI).—The acetate was first obtained by boiling a solution of the carbinol for seventeen hours with acetyl chloride and then distilling off the excess of the chloride. It is made much more easily directly from the magnesium derivative of the carbinol. Thus a solution of 25 g. of the ketone in benzene was added to an ethereal solution of phenyl magnesium bromide which contained 6.8 g. of magnesium. The mixture was kept for one hour at 50°, then cooled in a freezing mixture. Into the cooled solution was dropped a mixture of 33 g. of acetyl chloride and twice its volume of absolute ether. The brilliant red solution was allowed to reach the temperature of the room, then decomposed with ice and acid in the usual manner.

The ethereal layer was thoroughly washed with water, dried and concentrated. It yielded 10 6 g. of the same acetate that had been obtained from the carbinol. It was purified by recrystallization from chloroform and ether.

Anal. Calcd. for $C_{35}H_{28}O_2$: C, 87.5; H, 5.8. Found: C, 87.5; H, 6.2.

The acetate is readily soluble in benzene and in chloroform, very sparingly soluble in ether and in alcohol. It crystallizes in colorless plates and melts at 218°.

Oxidation.—A solution of one gram of the acetate and an equal weight of chromic acid in glacial acetic acid was heated on a steam-bath for about an hour, then cooled and

diluted with ice and ether. The ethereal layer was shaken with sodium carbonate, which extracted benzoic acid, then dried and evaporated. The residue when distilled with steam yielded 0.61 g. of pure benzophenone.

Summary

When tetraphenyl propenone reacts with phenyl magnesium bromide, the principal product is a diphenyl derivative which is formed by 1,4-addition to the system $-CO-C_6H_5$.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

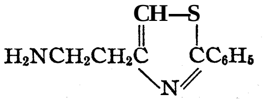
[CONTRIBUTION PROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE SYNTHESIS OF THIAZOLE AMINES POSSESSING PHARMACOLOGICAL INTEREST. V

BY W. S. HINEGARDNER[1] AND T. B. JOHNSON

RECEIVED AUGUST 8, 1930 PUBLISHED OCTOBER 6, 1930

In Paper IV of this series, Hinegardner and Johnson[2] have described the synthesis of 2-phenylthiazole-4-ethylamine, expressed structurally by formula I. This is a representative of a new type of aliphatic amines in which the thiazole nucleus has been substituted for a methylene *radical* in y-phenylpropylamine. It is a bridged thiazole compound of pharmacological interest and is only one of a series of compounds of its type which may be prepared by our method of synthesis. In this paper we describe a series of intermediate compounds which have been prepared in the development of a practical synthesis of 2-*p*-hydroxyphenylthiazole-4-ethylamine, XIV. This latter amine bears the same relationship to tyramine III as the thiazole amine I does to phenylethylamine II. It is a very potent substance biologically and its pharmacological activity is being investigated.



I

$C_6H_5CH_2CH_2NH_2$

II

$HOC_6H_4CH_2CH_2NH_2$

III

The starting points for our research were *sym.*-dichloro-acetone and the thioamide of anisic acid. These interact smoothly when warmed together in alcoholic solution, giving an excellent yield of the primary halide IV. Utilizing then the same technique as was described in our previous paper[B] for the preparation of the amine I, the various transformations recorded in Table I have been carried through successfully, leading up to the desired amine, XIV. The experimental data establishing the constitution and chemical identity of these various thiazoles are recorded in Table II.

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[1] Metz Research Fellow in Organic Chemistry, 1928–1929.

[2] Hinegardner and Johnson, THIS JOURNAL, 52, 3724 (1930).

TABLE I

NOMENCLATURE AND CONSTITUTION

IV	2-p-Methoxyphenylthiazole-4-chloromethyl	$ClCH_2T^aC_6H_4OCH_3$
V	Diethyl-2-*p*-methoxyphenylthiazole-4-methyl malonate	$(C_2H_5OOC)_2CHCH_2TC_6H_4OCH_3$
VI	2-p-Methoxyphenylthiazole-4-methyl malonic acid	$(HOOC)_2CHCH_2TC_6H_4OCH_3$
VII	2-p-Methoxyphenylthiazole-4-&propionic acid	$HOOCCH_2CH_2TC_6H_4OCH_3$
VIII	Ethyl-2-*p*-methoxyphenylthiazole-4-*β*-propionate	$C_2H_5OOCCH_2CH_2TC_6H_4OCH_3$
IX	2-*p*-Methoxyphenylthiazole-4-*β*-propionhydrazide	$H_2NNHCOCH_2CH_2TC_6H_4OCH_3$
X	2-p-Methoxyphenylthiazole-4-8-propionazide	$N_3COCH_2CH_2TC_6H_4OCH_3$
XI	Di-(2-*p*-methoxyphenylthiazole-4-ethyl)-*sym.*-urea	$CH_3OC_6H_4TCH_2CH_2NHCONHCH_2CH_2TC_6H_4OCH_3$
XII	2-p-Methoxyphenylthiazole-4-ethyl phthalimide	$C_6H_4(CO_2)NCH_2CH_2TC_6H_4OCH_3$
XIII	2-p-Methoxyphenylthiazole-4-ethylamine	$NH_2CH_2CH_2TC_6H_4OCH_3$
XIV	2-p-Hydroxyphenylthiazole-4-ethylamine	$H_2NCH_2CH_2TC_6H_4OH$

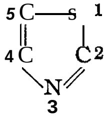
[a] T = Thiazole nucleus, 

TABLE II

EXPERIMENTAL DATA

Serial no.	Solvent	Yield, %	M.p., °C.	B.p., °C.	Crystal form	Nitrogen, % Calcd.	Nitrogen, % Found
IV	Pet. ether	72	55–56	185–188 (3 4 mm.)	Prisms	5.84	5.85 5.77
V	......	51.7	......	235–239 (3–4 mm.)	.....	3.85	3.78
VI[a]	Dil. alc.	85	97	.....	Prisms	4.56	4.48
VII	Alcohol	..	126–127	.....	Needles .	5.32	5.28
VIII	Alcohol	95	53–54	.....	.....	4.81	4.90
IX	Dil. alc.	95	158–159	.....	Needles	15.17	15.20
X	.....	94	78–79	.....	.....		
XI	Water	97.4	173–174	.....	Prisms or plates	11.35	11.30
XII	Alcohol	88	120–121	.....	Needles	7.69	7.63
XIII	.....	85	......	292–293 (3–4 mm.)	.....	11.96	12.08
XIV	.....	..	Hydrochloride, 218–222	.....	.....	Chlorine, 24.19	Chlorine, 23.85

[a] This acid crystallizes with two molecules of water.

Experimental Part

Thioanisamide was prepared according to the following series of reactions: anisic aldehyde ⟶ anisaldoxime ⟶ anisic nitrile (81%) ⟶ thioanisamide (88.8%). The reaction of this thioamide with dichloro-acetone is easily brought about by warming in alcohol solution, and the product of reaction IV can be purified by crystallization or distillation.

Preparation of the Malonate, V.—In the preparation of this ester we were not troubled with the formation of a disubstitution derivative of the malonic ester when the chloride IV was used as was observed in the first synthesis applied by Hinegardner and Johnson.[2] For this reason the yield of our primary malonic ester V was better than that in our previous work. Saponification of the ester and decarboxylation of the resulting malonic acid VI to form the propionic acid VII are easily accomplished by the usual organic technique and the yield in each operation is excellent. Formation of the hydrazide IX is brought about by refluxing the ester VIII in alcohol with 50% hydrazine hydrate solution. Complete transformation requires about twelve hours of digestion on a steam-bath.

Formation of the Amine XIII from Its Phthalimide.—The phthalimide XII is formed by heating the urea XI with phthalic anhydride at 220–225° as long as carbon dioxide is evolved. The imide is then decomposed by digestion in alcohol with 40% hydrazine hydrate solution and the amine XIII obtained in the form of its hydrochloric acid salt. Conversion of this methoxy compound into the free phenolic amine XIV was brought about by refluxing the base XIII for three hours with 48% hydrobromic acid solution. The amine XIV was obtained as an oil which showed no signs of solidifying on standing and was preserved in the form of its hydrochloric acid salt. Attempts to convert the urea XI directly into the amine XIV by digestion with 48% hydrobromic acid were unsuccessful.

Summary

1. *Sym.*-dichloro-acetone and thioanisamide interact in alcohol solution to form the compound 2-*p*-methoxyphenylthiazole-4-chloromethyl.
2. This halide has been incorporated into malonic ester and the resulting product converted by a standard series of reactions into a bridged thiazole derivative of tyramine, namely, 2-p-hydroxyphenylthiazole-4-ethylamine.
3. Eleven new thiazole compounds have been described.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE SYNTHESIS OF THIAZOLE AMINES POSSESSING PHARMACOLOGICAL INTEREST. VI

BY W. S. HINEGARDNER[1] AND T. B. JOHNSON

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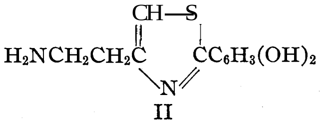
In the development of a practical method for synthesizing a bridged thiazole amine of the adrenaline type we undertook first the preparation of the thiazole amine expressed structurally by formula II. It was important, during the progress of our work, to compare the pharmacological activity of this base with that of 3,4-dihydroxyphenylethylamine I already described by Mannich and Jacobsohn.[2]

$(HO)_2C_6H_3CH_2CH_2NH_2$

I



II

The method of synthesis utilized by us for obtaining this interesting amine is an extension of the technique previously applied for the preparation of the corresponding bridged thiazole derivatives of phenylethylamine

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[1] Metz Research Fellow in Organic Chemistry, 1928–1929.

[2] Mannich and Jacobsohn, Ber., 43, 189 (1910); also J. *Chem. Soc.*, **97, 2254, 2257** (1911).

and tyramine. The starting points were vanillin and dichloro-acetone. The vanillin was first methylated according to the procedure of Barger and Silberschmidt,[3] and converted into the oxime of methylvanillin. Veratrol nitrile was then prepared and converted by the action of hydrogen sulfide into 3,4-dimethoxythiobenzamide. When this thioamide and dichloro-acetone were warmed together in alcohol solution, an immediate reaction took place with formation of the primary halide, 2-(3,4-dimethoxyphenylthiazole)-4-chloromethyl, III, in excellent yield.

TABLE I

NOMENCLATURE AND CONSTITUTION

III	2-(3,4-Dimethoxyphenylthiazole) 4-chloromethyl	$ClCH_2TC_6H_3(OCH_3)_2$
IV	Diethyl 2-(3,4-dimethoxyphenylthiazole)-4-methyl malonate	$(C_2H_5OOC)_2CHCH_2TC_6H_3(OCH_3)_2$
V	2-(3.4-Dimethoxyphenylthiaaole-4-methyl-malonic acid	$(HOOC)_2CHCH_2TC_6H_3(OCH_3)_2$
VI	2-(3,4-Dimethoxyphenylthiazole)-4-β-propionic acid	$HOOCCH_2CH_2TC_6H_3(OCH_3)_2$
VII	Ethyl 2-(3.4-dimethoxyphenylthiazole)-4-8-propionate	$C_2H_5OOCCH_2CH_2TC_6H_3(OCH_3)_2$
VIII	2-(3,4-Dimethoxyphenylthiazole) 4 β-propionhydrazide	$H_2NNHCOCH_2CH_2TC_6H_3(OCH_3)_2$
IX	2-(3,4-Dimethoxyphenylthiazole)-4-β-propionazide	$N_3COCH_2CH_2TC_6H_3(OCH_3)_2$
X	Di-2-(3,4-dimethoxyphenylthiazole)-4-ethyl-*sym.*-urea	$(CH_3O)_2C_6H_3TCH_2CH_2NHCONHCH_2CH_2TC_6H_3(OCH_3)_2$
XI	2-(3,4-Dimethoxyphenylthiazole)-4-ethyl phthalimide	$C_6H_4(CO)_2NCH_2CH_2TC_6H_3(OCH_3)_2$
XII	2-(3,4-Dimethoxyphenylthiazole)-4-ethylamine	$NH_2CH_2CH_2TC_6H_3(OCH_3)_2$
XIII	2-(3.4-Dioxyphenylthiazole)-4-ethylamine	$NH_2CH_2CH_2TC_6H_3(OH)_2$

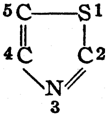
T = Thiazole nucleus 

TABLE II

EXPERIMENTAL DATA

Serial no.	Solvent	Yield, %	M. p., °C.	B. p., °C.	Crystal form	Nitrogen, % Calcd.	Nitrogen, % Found
III	Benzene, ligroin	74	89–90	.....	Prisms	5.19	5.30 5.22
IV	.....	53	.....	251–255 (2–3 mm.)	.....	3.56	3.63
V[a]	Alcohol	80	141	.....	Prisms	4.15	4.10
VI	Alcohol	80	94	.....	Needles	4.78	4.74
VII	Alcohol	81	69	220–223 (3 mm.)	Needles	4.36	4.39
VIII	Alcohol	94	162	.....	Needles	14.0	13.8
IX	.....	90	77–78	.....	.....	..	...
X	Alcohol, water	90	165–166	.....	Plates	10.11	10.00
XI	Alcohol	72	143–144	.....	Needles	7.11	7.03
XII	Alcohol	52	Di-hydrochloride 225–227 55	210–212 (4 mm.)	..... Cl,	10.6 21.03	10.5 20.75

[a] This acid crystallizes with one molecule of water.

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[3] Barger and Silberschmidt, *J. Chem. Soc.*, 133, 2924 (1928).

The different steps of the synthetic process leading up to the amine construction XIII are shown in Table I. The yields in each step are very favorable, and the intermediate compounds can be easily obtained in a high degree of purity.

The conversion of the dimethyl ether represented by formula XII into the amine XIII has not, thus far, been accomplished successfully. Demethylation of this thiazole by the action of hydriodic and hydrobromic acids leads to the formation of the base XIII, but this has not been obtained thus far in a state of purity. For this reason no constants for this compound are reported. The study of this interesting compound and several of its derivatives is being continued. The experimental data characterizing the different thiazoles prepared are recorded in Table II.

Experimental Part

3,4-Dimethoxythiobenzamide $(CH_3O)_2C_6H_3CSNH_2$.—This was prepared by heating veratrol nitrile with an alcohol solution of hydrogen sulfide in an iron bomb at 100° and was easily obtained in a yield of 90% of the theoretical. The amide crystallizes from alcohol in the form of prisms or needles melting at 183°. It is difficultly soluble in alcohol, acetone and benzene and practically insoluble in water. Alcohol is the best solvent for crystallization.

Anal. Calcd. for $C_9H_{11}O_2NS$: N, 7.10. Found: N, 7.08, 7.02.

Preparation of the Hydrazide, VIII.—This is easily obtained by heating the propionate VII in alcohol solution with the required amount of 40% hydrazine hydrate solution for twelve to fifteen hours. Conversion to the corresponding azide is accomplished by diazotization in acetic acid solution. This compound is a very unstable compound when heated above its melting point. By warming the azide in dilute acetic acid solution, almost the theoretical yield of the urea X is obtained. The following steps of the synthesis leading up to the amine XII from this urea do not present any experimental difficulties.

Demethylation of the Amine, XII.—Thus far, conversion of this compound into the hydroxyl compound XIII has not been accomplished successfully. Refluxing with hydriodic and hydrobromic acids leads to complete demethylation, but the base formed is very susceptible to oxidation and the solutions take on a very dark color during the digestion process. Neutralization of the hydrobromic acid solution by potassium hydroxide causes separation of the amine as an oil, which dissolves immediately when the solution is made alkaline. The base was extracted with ether and dried over sodium sulfate. On evaporating the solvent, a brown resinous substance was obtained which could not be distilled without decomposition and also showed no signs of crystallization. Further attempts are being made to purify this base and separate it if possible in the form of its hydrochloride.

Summary

1. 3,4-Dimethoxythiobenzamide has been prepared. This interacts smoothly with dichloro-acetone to form 2-(3,4-dimethoxyphenylthiazole)-4-chloromethyl.

2. This chlorothiazole compound has been transformed by a series of standardized reactions into the new bridged thiazole amine 2-(3,4-di-

methoxyphenylthiazole)-4-ethylamine. The further study of this base is being continued with the object of developing a practical synthesis of the bridged thiazole derivative of 3,4-dihydroxyphenylethylamine represented by formula II in this paper.

3. Ten new thiazole derivatives have been described.

NEW HAVEN, CONNECTICUT

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

STUDIES ON THE POLYMETHYLBENZENES. IV. THE PREPARATION AND PHYSICAL PROPERTIES OF PURE PSEUDOCUMENE[1]

BY LEE IRVIN SMITH AND AXEL P. LUND

RECEIVED AUGUST 11, 1930 PUBLISHED OCTOBER 6, 1930

The work reported in this paper is a continuation of a research which has for one of its immediate purposes the separation of the isomeric liquid hydrocarbons which result from the methylation of xylene by the method of Friedel and Crafts.[2] In the previous papers reports were made on the pure tetramethylbenzenes, and on penta- and hexamethylbenzenes. This paper deals with pseudocumene (1,2,4-trimethylbenzene), and reports the preparation and purification, together with the freezing point, refractive index and vapor pressure curve of a very pure sample.

Pseudocumene has been obtained from petroleum,[3] but the commercial source is coal tar.[4] However, pseudocumene obtained in this way is always contaminated with mesitylene, and it is very doubtful whether a specimen of the pure hydrocarbon has ever been obtained from any of these sources.

Synthetic pseudocumene has been made in several ways, but the yields were always low and, in addition, most of the methods are open to the objection that isomeric by-products might result. Thus Jacobsen[5] reports that if phorone is heated with phosphorus pentoxide or zinc chloride, some pseudocumene results, but if concd. sulfuric acid be used, only mesitylene results. The decomposition of camphor by zinc chloride is reported to give pseudocumene[6] but these syntheses do not give pure products, nor good enough yields for purposes of preparation.

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[1] Abstracted from a thesis by Axel P. Lund, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Master of Science.

[2] Smith and co-workers, I, THIS JOURNAL, 51, 2994 (1929); II, 51, 3001 (1929); III, 52, 1998 (1930); also 48, 1413 (1926).

[3] Engler, *Ber.*, 18, 2234 (1885); Markownikow, *Ann.*, 234, 97 (1886).

[4] Jacobsen. *Ber.*, 9, 256 (1876); *Ann.*, 184, 179 (1877); Schultz and Herzfeld, *Ber.*, *42*, 3602 (1909).

[5] Jacobsen, *ibid.*, 10, 855 (1877).

[6] R. Fittig, Köbrich and Jilke, *Ann.*, 145, 140 (1868); Reuter, *Ber.*, 16, 626 (1883).

Paul Jannasch, and others[7] have prepared pseudocumene by treating bromoxylenes with methyl iodide and sodium, or by treating dibromotoluenes with the same reagents, but in every case there is question as to the purity of the aromatic bromo compounds, and the yields of pseudocumene were very low.

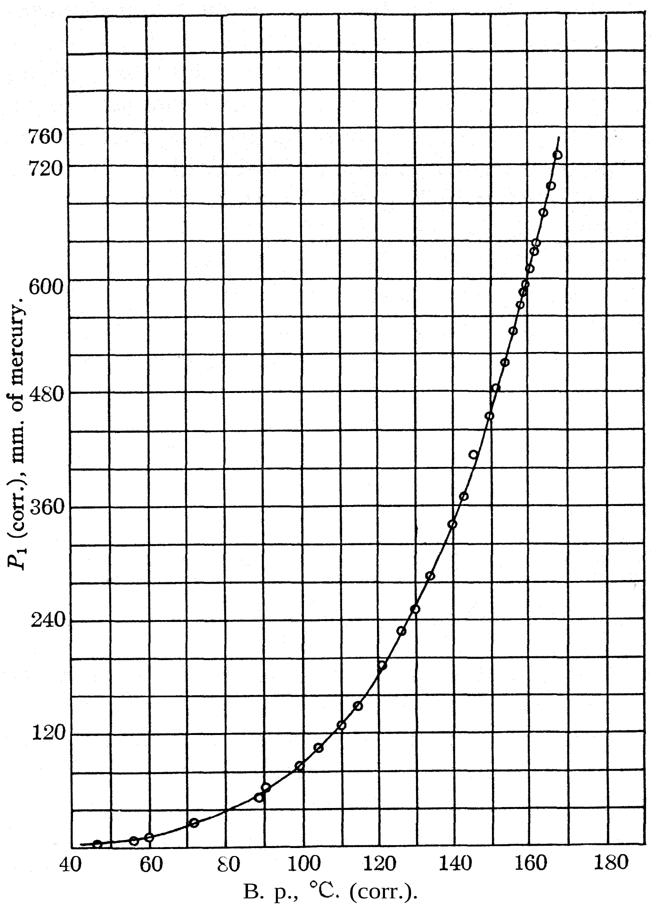

Fig. 1.—Vapor pressure curve for pseudocumene.

While the direct methylation of the xylenes using aluminum chloride and methyl chloride has been used to prepare pseudocumene, such a method always gives a mixture and none of the specimens prepared in this way were pure. This is because the methylation in the presence of aluminum chloride is reversible, and methyl groups are eliminated as well as intro-

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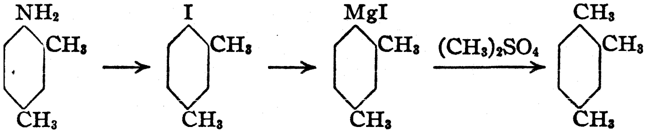
[7] Jannasch, *Ann.*, **176**, 283 (1875); E. and R. Fittig, *ibid.*, 139, 187 (1866); R. Fittig and Laubinger, *ibid.*, **151**, 258 (1869); R. Fittig and Jannasch, *ibid.*, 151, 291 (1869); Jannasch, *ibid.*, 176, 283 (1875).

duced, so that the final result will depend upon many factors; but in every case the product is a mixture of substances, and very little is known about the way in which various factors influence the result. About the only generalization that can be safely made is that ortho methylation apparently occurs in very small amounts: that is, of the trimethylbenzenes formed, very little will be the 1,2,3-isomer, and of the tetramethylbenzenes, the 1,2,3,4-isomer will result in least amount.[8]

The one synthesis in the literature which might be made to give pure pseudocumene in fair yields is that of Haller,[9] who started with pseudocumidine, a solid, which could be obtained in a pure state. This was diazotized, and then reduced to the hydrazine, after which the hydrazine group was eliminated by boiling with a solution of copper sulfate. Haller gives the boiling point of his product as 169–170° (corr.), but does not mention the over-all yield nor the amount of material he prepared. His synthesis was used to prepare pseudocumene in 1919 by Auwers,[10] who gave the boiling point as 169° and n_{D}^{20} as 1.5046.

All the other samples of pseudocumene which have been used for the determination of physical constants were commercial products, and nothing is known as to their method of preparation.[11]

Preparation of Pseudocumene.—The preparation of pseudocumene for this work involves the following series of reactions



Starting with pure xylidine, the series gives intermediates which. are easily purified. No rearrangements are involved, and the only trimethylbenzene which can result from these reactions is pseudocumene. Some xylene is formed, due to the reducing action of the Grignard reagent, but this is easily separated by fractional distillation.[12]

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[8] See papers I, II and III in this series; also Smith and Dobrovolny, THIS JOURNAL, 48, 1420 (1926); Friedel and Crafts, Ann *chim.* phys., 1, 449 (1884); Ador and Rilliet, *Ber.*, 11, 1627 (1878); 12, 329 (1879); Jacobsen, *ibid.*, 9, 256 (1876); 10, 1009 (1877); 14, 2624 (1881); 18, 338 (1885).

[9] Haller, ibid., 18, 89 (1885).

[10] Auwers, Ann., 419, 99 (1919).

[11] (a) Auwers and Müller, *Ber.*, 44, 1606 (1911); (b) Landolt and John, *Z. physik. Chem.*, 10, 303 (1892); (c) Brühl, J. prakt. *Chem.*, [2] 50, 142 (1894); (d) Perkin, J. Chem. *Soc.*, 67, 1249 (1896); (e) Woringer, *Z. physik.* Chem.. 34, 263 (1900).

[12] While this paper was being written, the paper of Maxwell and Adams [THIS JOURNAL. 52, 2962 (1930)] appeared, in which these authors prepared pseudocumene from m-xylene by bromination, followed by conversion of the bromo-*m*-xylene to pseudocumene through the Grignard reagent. Their yield of pseudocumene, based upon the m-xylene, was about 40%, as compared with our over-all yield of about 30%.

Experimental Part

4-Amino-1,3-dimethylbenzene.—This was obtained from the Eastman Kodak Co., and was distilled immediately before using; b. p. 111° at 18 mm. Practically all of the sample showed a constant boiling point.

4-Iodo-1,3-dimethylbenzene.[13]—In a 3-liter round-bottom flask are placed 200 g. of concd. sulfuric acid, 1500 cc. of water and 121 g. (1 mole) of xylidine. The mixture is warmed on the steam-bath until all of the xylidine sulfate dissolves, and is then cooled to 0°, with stirring to produce small crystals. To the cold solution is added a solution of 69 g. of sodium nitrite in 200 cc. of water with stirring and cooling. (The temperature should not be allowed to rise above +5°.) An excess of nitrous acid should be used, and after about 80% of the sodium nitrite is added, the starch–potassium iodide test should be applied. It should be positive for fifteen minutes after an excess of sodium nitrite has been added. When enough sodium nitrite has been supplied, a solution of 250 g. of potassium iodide (30% excess) in 300 cc. of water is gradually run in, with stirring and cooling. The temperature of the mixture is kept at 5–10° for twenty-four hours and then allowed to come to room temperature. The iodo compound settles to the bottom as a black, oily layer. The mixture is allowed to stand for a day at room temperature, and is finally warmed on the steam-bath until effervescence ceases. The mixture is then made strongly alkaline, stirred and the aqueous layer siphoned off. The dark oil is again treated with alkali, after which it is steam distilled. The orange colored oil is separated from the water, dried over calcium chloride and distilled *in vacuo;* b. p. 105–106° at 5 mm.; 108–110° at 10–12 mm.; 124–126° at 28–30 mm. Runs were made in 0.5, 1.0, 1.5 and 2.0 molar quantities, the yields running from 69.0 to 82.7%, with an average yield of about 75% for 1.0 molar quantities. Two important factors which influence the yields very much are the amount of potassium iodide used and the time of the reaction. An excess of about 30% of potassium iodide and very slow raising of the temperature after the potassium iodide has been added give the best yields.[14]

Pseudocumene.—The iodoxylene was converted to pseudocumene using the method already described for the preparation of isodurene.[15] The product is worked up in the same way: the excess diiethyl sulfate is destroyed with alcoholic alkali and, after washing out the alcohol and alkali, the oil is dried over calcium chloride and then warmed with sodium shavings to remove the last traces of halogen compounds. The oil is then filtered from the sodium and distilled in *vacuo* using a long packed column with a double jacket. Grignard reactions were carried out using 0.5 to 3.0 molar quantities, but the yields do not differ very much from the smaller to larger runs. The material from six different runs, totaling $11^3/_8$ moles of iodo compound, was combined and fractionated three times, with the results shown in Table I.

TABLE I

FRACTIONATION OF CRUDE REACTION PRODUCT

Fraction	B. p., °C.	Pressure, mm.	Wt., g.	Yield, %
I m-Xylene	Up to 45	16	346	28.5
II Intermediate	47.7–67.2	21–22	18	..
III Pseudocumene	68–68.5	22	503	37
IV Residue in flask	....	...	Very small	..

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[13] See also Hammerich, *Ber.*, 23, 1634 (1890); Willgerodt, *ibid.*, 33, 842 (1900).

[14] It is very interesting in this connection that we were unable to make the corresponding bromo compound from xylidine using the Sandmeyer reaction. The product is chiefly xylenol and the yield of bromo compound is very small.

[15] Smith and MacDougall, THIS JOURNAL, 51, 3003 (1929); Smith, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1931, Vol. XI.

About a third of the material is lost in the synthesis, probably as m-xylene which is very difficult to hold in a receiver under vacuum. That Fraction I is m-xylene was shown by converting a sample of it to the dinitro compound, m. p. 92–93°, and the trinitro compound melting at 181.5–182°.

In order to get a very pure sample for the determination of physical constants, Fraction III was refractionated, cutting off the first and final fourths and taking only the middle half. Then the process was repeated, using as starting material the middle half from the previous fractionation, and again cutting off the first and final fourths. This gave 125 g. of pseudocumene having a constant boiling point of 68.0° at 22 mm., but all the fractions of the pseudocumene boiled over a range of about 0.5°.

A further attempt to purify the hydrocarbon by making the picrate and recrystallizing this was a failure because the picrate of the substance is too soluble and has too low a melting point to be of any use for purification purposes.

The Vapor Pressure Curve of Pseudocumene.—There is, apparently, only one study on the vapor pressure of pseudocumene in the literature, that of Woringer,[16] and all the data on the vapor pressure of this substance in the literature are copied from Woringer's paper.[17]

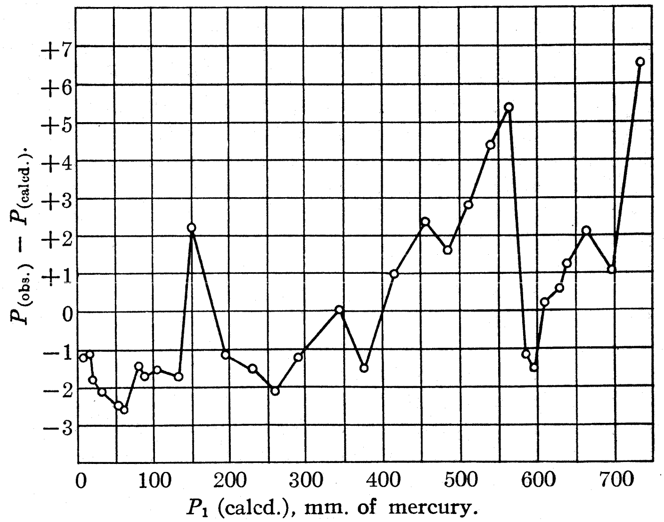

Fig. 2.—Vapor pressure–deviation plot for pseudocumene. $\text{Log}_{10}p = 7.0144 - 1.5014\mu - 0.1447\mu^2$. ($\mu = 1000/T_{\text{abs.}}$)

The method used for determining the vapor pressure curve is a dynamic one, and the apparatus and procedure have already been described.[18] The results are given in the form of tables and curves. The equation

$$\log_{10} p = 7.0144 - 1.5014\mu - 0.1447p^2 \text{ (where } \mu = 1000/T)$$

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[16] Woringer, Z. *physik.* Chem., 34, 263 (1900).

[17] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. III, p. 225; Spielmann, "The Constituents of Coal Tar," Longmans, Green & Co., New York, 1924, p. 62.

[18] MacDougall and Smith, This Journal, 52, 1998 (1930).

fits these results fairly well. For comparison, the calculated and observed vapor pressures are given in the table, and the deviations are shown in the form of a graph. In every case Woringer's boiling points are lower than ours, and in the region from 5 to 100 mm. pressure Woringer's boiling points are too low by as much as 50" in extreme cases. In the region of higher pressures, Woringer's boiling points agree fairly well with ours, but are always too low, approaching ours more closely the higher the pressure.

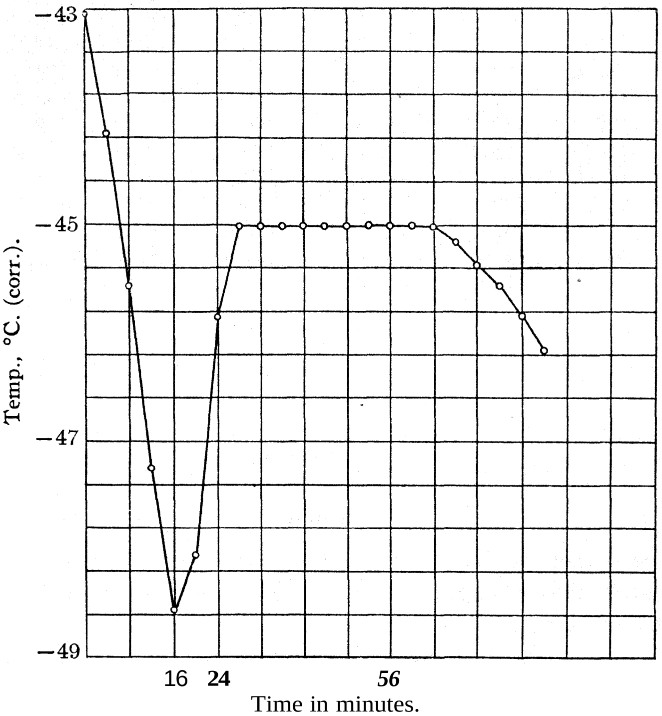

Fig. 3.—Cooling curve, freezing point of pseudocumene.

The boiling point of pseudocumene under 760 mm. pressure is 169.34°, calculated from the vapor pressure equation, and 169.1" by extrapolation of the vapor pressure curve.

The Freezing Point of **Pseudocumene.**—This was determined essentially as described in connection with previous work.[19] The cooling bath was composed of chlorobenzene (freezing point −45°) to which was added carbon dioxide snow and ether until the bath was at −60°. Once this temperature was reached, it was easy to maintain it by adding small amounts of ether and solid carbon dioxide from time to time. Readings were taken every minute and the results are shown graphically in Fig. 3. The freezing point of pseudocumene is —45.00 ± 0.05" corr.

[19] Smith and MacDougall, THIS JOURNAL, 51,3005 **(1929).**

TABLE II

VAPOR PRESSURE DATA FOR PURE PSEUDOCUMENE

B. p., °C. (corr.)	P, obs. (mm.)	P, calcd.	Deviation	B. p., °C. (corr.)	P, obs. (mm.)	P, calcd.	Deviation
47.1	7	8.207	−1.207	143.3	373.7	375.2	−1.5
57.6	13	14.16	−1.16	147.0	417.2	416.2	+1.0
61.6	15.5	17.27	−1.77	150.1	458.2	455.8	+2.4
73.1	28.0	30.09	−2.09	152.1	483.7	482.1	+1.6
89.1	56.0	58.37	−2.37	154.4	516.2	513.4	+2.8
92.0	63.0	65.55	−2.55	156.2	543.7	539.3	+4.4
98.6	83.0	84.70	−1.7	158.1	573.3	567.9	+5.4
99.6	86.5	87.96	−1.46	159.2	583.8	584.9	−1.1
105.0	106.0	107.5	−1.5	159.9	594.3	595.8	−1.5
111.1	132.0	133.7	−1.5	160.9	612.3	612.1	+0.2
115.1	152.5	150.1	+2.4	161.9	628.8	6282	+0.6
122.6	196.6	197.7	−1.1	162.3	636.3	635.0	+1.3
127.7	231.6	233.1	−1.5	164.3	669.8	667.7	+2.1
130.8	255.1	257.2	−2.1	165.9	698.8	697.6	+1.2
134.9	290.6	291.9	−1.3	167.8	738.8	732.3	+6.5
140.1	341.6	341.5	+0.1				

Refractive Index.—Previous determinations, recorded in the literature, for the refractive index of pseudocumene are Auwers,[10] n_D^{20} 1.5046; Auwers and Müller,[11a] $n_D^{13.9}$ 1.50780; Landoldt and John,[11b] $n_D^{14.7}$ 1.5072; and Brühl,[11c] $n_D^{21.6}$ 1.50441. All our fractions of pseudocumene, after the second distillation, gave the value n_D^{24} 1.5032 (Abbé refractometer).

Summary

1. A new method has been devised for preparing pseudocumene in quantity and fairly cheaply. The method gives a product free from any isomeric by-products.

2. The vapor pressure curve, freezing point and refractive index of a very pure specimen of pseudocumene have been determined.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE ACTION OF HEAT ON ETHYLAMINE AND BENZYLAMINE

BY CHARLES D. HURD AND FLOYD L. CARNAHAN[1]

RECEIVED AUGUST 11, 1930 PUBLISHED OCTOBER 6, 1930

The only primary aliphatic amines whose pyrolysis has been studied are ethylamine and propylamine. The former has been investigated at 500, 700 and 1000° over kaolin by Upson and Sands.[2] At the lower temperatures the major primary reaction is the formation of acetonitrile and hydrogen, along with the not inappreciable production of ethylene and ammonia. The products at 1000° are stated to be hydrogen, nitrogen and butane. Müller[3] found that at 1240° the products are hydrogen cyanide and methane. From n-propylamine at 700°, Upson and Sands obtained propionitrile, hydrogen cyanide, ammonia, ethylene, propylene, hydrogen and nitrogen.

In the present investigation, an experiment with ethylamine at 600° was carried out but our major interest was at higher temperatures. Several runs were made at 890–900° (furnace temperature of 980°), and in these the contact time was varied from one second to 300 seconds.

Acetonitrile was found at 600° but not at 900°. Hydrogen cyanide was always present at the higher temperature, but only a small amount of ammonium cyanide was noticed when the contact time was in excess of one minute. No cyanogen was formed whatsoever. The effect of contact time on the yield of ethylene at 900° is marked. With a contact time of one second the ethylene content of the gases was 10.3%; with 15.5 seconds, 5.0%; with eighty seconds, 0.5%; and with longer durations, no ethylene at all. This agrees with Bone and Coward's[4] statement that ethylene is nine-tenths decomposed in one minute at 950°, chiefly into methane and hydrogen.

In experiments with a kaolin-packed tube (as in Upson and Sands' experiments), the formation of appreciable volumes of carbon monoxide was observed. This is not a new type of observation for Bone and Cowards noticed carbon monoxide formation in the high-temperature pyrolysis of methane in a porcelain tube. These authors mention that it is impossible to avoid reduction of the porcelain by carbon at temperatures above a red glow.

In the theoretical treatment of Upson and Sands' paper it is stated that the primary dissociation of ethylamine yields the ethylidene radical and ammonia: $CH_3CH_2NH_2 \longrightarrow CH_3CH= + NH_3$. The ethylidene was regarded as the precursor of ethylene (by rearrangement), of ethane (by

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[1] Du Pont Fellow during 1929–1930.

[2] Upson and Sands, THIS JOURNAL, 44, 2306 (1922).

[3] Müller, *Bull. soc. chim.*, [2] 45, 439 (1886).

[4] Bone and Coward, *J. Chem. Soc.*, 93, 1216 (1908).

[5] Ref. 4, p. 1206.

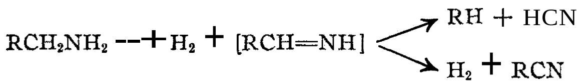
hydrogenation) and of butane. Regarding the latter it is stated: "Butane was the chief hydrocarbon formed at 1000°. This must have been formed by the union of 2 ethylidene radicals and 2 atoms of hydrogen as in the Wurtz reaction: $2CH_3CH{=} + 2H \longrightarrow C_4H_{10}$."

The data of Upson and Sands appear to show that at 1000° 32.9 g. (26.9 g. C and 6.0 g. H) of butane was formed per 100 g. of ethylamine decomposed. To be sure, the stated ratio of 26.9 g. C to 6.0 g. H, or 4.48 to 1, corresponds fairly well to the value for butane which is 4.8 to 1. However, it agrees even more closely to the C–H ratio in propane, which is 4.5 to 1. Because of subsequent work wherein it has been demonstrated that both n- and *i*-butane are rapidly decomposed[6] at temperatures far below 1000°, namely, at 650–700°, it seemed to us that this recorded synthesis of butane from ethylamine at 1000° was of sufficient theoretical importance to merit further study.

In our work butane was searched for under a wide variety of conditions at 900–1000° but none was ever found. Attempts to condense it at −78° from the gaseous products were fruitless, though butane had been shown to condense in this manner even if highly diluted. Furthermore, in our analyses of the paraffin gases of the reaction, methane rather than butane was indicated. The value of n in the hydrocarbon formula, C_nH_{2n+2}, was only slightly greater than unity (1.02–1.15).

Benzylamine.—Benzylamine was subjected to different temperatures for various lengths of time. Its stability is evidenced by the fact that heating at 275–300° for several hours produced no change. It was also found to be stable at 545° with a contact time of about one minute With the use of a temperature of 630° and a contact time of 160 seconds, pyrolysis into benzene, toluene, benzonitrile, hydrogen cyanide and ammonia was effected. Much unchanged benzylamine was apparent when a contact time of forty-nine seconds at 700° was chosen. The other products were benzene, toluene, gas and only a trace of benzonitrile.

Mechanism of the Pyrolysis.—In certain respects the behavior of ethylamine and benzylamine at high temperatures is strictly comparable. The formation of acetonitrile and hydrogen from the former is analogous to the production of benzonitrile and hydrogen from the latter. So also, the formation of methane, hydrogen cyanide and hydrogen from ethylamine has its parallel (in benzylamine) in the production of benzene, hydrogen, cyanide and hydrogen. Both of these processes may be considered to proceed through an intermediate aldimide, $RCH{=}NH$, wherein R represents methyl or phenyl.



$$\mathrm{RCH_2NH_2} \longrightarrow \mathrm{H_2} + [\mathrm{RCH{=}NH}] \begin{cases} \nearrow \mathrm{RH} + \mathrm{HCN} \\ \searrow \mathrm{H_2} + \mathrm{RCN} \end{cases}$$

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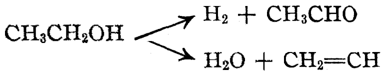
[6] Pease, This Journal, *50*, 1779 (1928); Hurd and Spence, *ibid.*, 51, 3353 (1929).

Hydrogen escapes in part but presumably only in part. Reaction with unused amine would give rise to ammonia and either ethane or toluene

$$\mathrm{RCH_2NH_2} + 2\mathrm{H} \longrightarrow \mathrm{RCH_3} + \mathrm{NH_3}$$

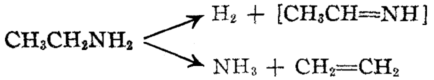
both of which were observed. Further reduction[7] of the $\mathrm{RCH_3}$ into RH (methane or benzene) and $\mathrm{CH_4}$ would also follow in part.

Ethylamine is "ammono-ethyl alcohol." The analogies in the water and the ammonia system of compounds may be extended to the field of pyrolysis. Alcohol, on pyrolysis, undergoes reactions[8] of dehydration and of dehydrogenation



$$\mathrm{CH_3CH_2OH} \begin{array}{l} \nearrow \mathrm{H_2 + CH_3CHO} \\ \searrow \mathrm{H_2O + CH_2{=}CH_2} \end{array}$$

Ammono-ethyl alcohol may be expected to undergo similar reactions of deammonation and of dehydrogenation



$$\mathrm{CH_3CH_2NH_2} \begin{array}{l} \nearrow \mathrm{H_2 + [CH_3CH{=}NH]} \\ \searrow \mathrm{NH_3 + CH_2{=}CH_2} \end{array}$$

The dehydrogenation reaction, leading to the aldimide and eventually to cyanides, has already been discussed. Equally representative of fact is the deammonation reaction, of which ethylene is an important reaction product.

Benzyl alcohol and benzylamine are analogous compounds in the two systems. The former cannot lose water unimolecularly without changing into the phenylmethylene radical. This it evidently does not do since stilbene is not formed. Bimolecular dehydration into dibenzyl ether or its pyrolytic products (toluene and benzaldehyde) is the reaction which has been recorded.[9] Similarly, no test for stilbene could be obtained in the pyrolysis of benzylamine. With no evidence for the phenylmethylene radical from this source, it seems equally unnecessary to postulate the ethylidene radical from the ethylamine pyrolysis. For a bimolecular deammonation of benzylamine, dibenzylamine or its decomposition products (toluene and iminobenzaldehyde) would be anticipated. Traces of a secondary amine were realized but the high temperature of the reaction practically excluded the possibility of the synthesis of dibenzylamine. The decomposition of the aldimide, which may thus be formed from dibenzylamine or directly from benzylamine, into benzene and hydrogen cyanide is evidently more rapid than the alternative decomposition into benzonitrile and hydrogen, since only traces of benzonitrile were among the decomposition products from a run at 700° with a contact time of forty-nine seconds. At 630° and

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[7] Cobb and Dufton, Gas World, 69, 127 (1918); Fischer and Schrader, *Brennstoff Chem.*, 1, 22 (1920); Hurd and Spence, THIS JOURNAL, 51,3569 (1929).

[8] Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., New York, 1929, p. 150.

[9] Lachman, THIS JOURNAL, 45,2358 (1923).

TABLE I

PYROLYSIS OF ETHYLAMINE

Run number	2	3	4	5	6	7	8	9	10	11
Size of sample, g.	7.0	3.5	7.0[d]	5.6	10.5[h]	10.5	10.5	10.5	10.5	9.8
Tube filling	None[f]	None"		[k]	[k]	[k]	Kaolin cubes	Kaolin cubes	Kaolin cubes	None
Inside temp., °C.	600[b]	890	890	895	890	890	900	900	900	900
Contact time, sec.	300	122	130	162	23.2	15.5	77	81	84	1.08
CH_3CN and NH_4CN formed, g.	2.25'	..	..	0.25[j]	..	3.4[e]	0.16	0.34	0.21	3.35"
Gas collected (S. T. P.), cc.	1760	2060	5870	2940	7540	4950	8640	10,200	10,800	7640
Gas analysis, % by volume										
Hydrogen	52.1	51.2	76.2	72.4	70.1	51.6	60.9	73.2	74.4	50.2
Unsatd. hydrocarbons	None	None	None	None	0.6	5.0	0.5	None	0.7	10.3
Paraffins	4.9	16.8	11.2	3.7	2.8	3.2	12.8	9.4	6.6	33.0
							$n = 1.15$	$n = 1.02$	$n = 1.15$	$n = 1.02$
Carbon monoxide	None	None	None	None	None	None	5.0	5.9	5.9	1.0
Nitrogen	39.3'	30.0'	9.6	22.3	26.3	39.2	17.3	9.3	11.2	3.7
Gases liquefied at −80°, g.	0.2'	1.0[l]	Not used	0.0	0.0	0.0	0.0	...	0.0	0 0
Calcd. weight of products from 100 g. of ethylamine, g.										
Unsatd. hydrocarbons (as C_2H_4)	..	..	..	..	0.54	2.94	0.52	None	0.90	10.0
Hydrogen	1.17	2.71	5 74	3.51	4.52	2.18	4 50	6.37	6.85	3.52
Nitrogen	..	..	10 00	14.7	23.6	23.1	17.8	11.3	14.4	3 43
Satd. hydrocarbons (as CH_4)	0.88[c]	707"	6.69[c]	1.39"	1.43[c]	1.08[c]	8.52	6.65	5.50	18.78
Carbon monoxide	..	..	..	..	..	..	5.14	7.15	7.60	0.97

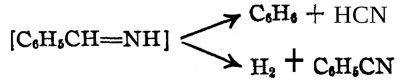
[a] An iron thermocouple sheath was used in this run. It seemed to cause considerable carbonization, and was accordingly omitted in later runs. [b] Indicates outside temperature. [c] Calculated as methane. [d] A negative search was made for cyanogen in this run. The off-gas was passed through concentrated hydrochloric acid. No precipitate was formed as is the case with even traces of cyanogen. [e] Mostly ammonium cyanide. [f] A small amount of tar was formed in the reaction tube. [g] Not freed from the nitrogen used before the run. [h] In this and in the following runs considerable carbonization was noted. [i] This consisted of 2.0 g. CH_3CN and 4.25 g. NH_4CN. [j] This is all NH_4CN. [k] The filliig here consisted of porcelain chips coated with kaolin. [l] This condensate boiled above room temperature and thus was not butane.

160 seconds, however, benzonitrile was an important product. With ethylamine, a similar phenomenon was noticed, for the proportionate yield of methane was far greater in a run of 900° and one second than at 900° and fifteen seconds.

Thus, the primary equations for the pyrolysis of benzylamine may be summarized as follows

$$C_6H_5CH_2NH_2 \longrightarrow H_2 + [C_6H_5CH{=}NH]$$
$$2C_6H_5CH_2NH_2 \longrightarrow NH_3 + C_6H_5CH_3 + [C_6H_5CH{=}NH]$$

These reactions are followed by reduction and by decomposition of the aldimide



$$[C_6H_5CH{=}NH] \begin{array}{l} \nearrow C_6H_6 + HCN \\ \searrow H_2 + C_6H_5CN \end{array}$$

Experimental Part

Ethylamine.—The data obtained from pyrolysis of ethylamine are shown in Table I. One experiment at an "outside temperature" of 500" is not listed, since no pyrolysis occurred. A brief summary of experimental details will serve to make clear the means of arriving at these results.

Apparatus.—An empty pyrex tube was used for the decomposition of ethylamine at 500 and at 600°. For the 890–900° temperatures a quartz tube of 2 cm. diameter was employed. In Run 11 a quartz tube with a diameter of 0.55 cm. was used in order to obtain a short time of contact. The temperatures were obtained by the use of a potentiometer and a calibrated chromelalumel thermocouple. In one instance an iron thermocouple sheath was present, but it was omitted in later runs on account of its tendency to increase carbonization. In four runs a filling of porcelain chips coated with kaolin was present; in three runs small cubes of kaolin were used. An ordinary gas combustion furnace was suitable for the lower temperatures but a Hoskins electric furnace with an effective heating length of 25 cm. was used in the vicinity of 900°.

Liquid ethylamine was pushed into the reaction tube from a 25-cc. graduated capsule in an ice-salt bath by displacement with mercury. In this manner the rate of feed could be easily controlled. The off gas first passed through a U-tube cooled in an ice–salt bath to about −10°. This served to collect ammonium cyanide, acetonitrile and the greater part of any unchanged amine. Next in the train was a gas washing bottle containing 200 cc. of hydrochloric acid of such concentration as to be equivalent to more than the total base used. The gases were then dried by passing them through a 15-cm. calcium chloride drying tower and a U-tube containing dehydrite. To condense any butane in the previously dried gases, a spiral condenser held at −78° by a mixture of acetone and solid carbon dioxide in a Dewar flask was used. This condenser was so constructed that any condensate could be volatilized and analyzed as a gas. It is of the type described by H. S. Davis.[10] Under the conditions used, butane could be readily condensed from 2-liter samples containing 10% by volume and detected as a liquid when only 5% was present. Finally, the residual gas was collected over water in 2.5-liter bottles. The connections used were of rubber tubing with extra heavy walls.

Procedure.—The ethylamine was Eastman's anhydrous product. The filling used in Runs 4 to 7, inclusive, was prepared by wetting porcelain chips and rolling them in kaolin. The filling for Runs 8 to 10, inclusive, was made by grinding kaolin into a stiff paste with water, spreading it on a plate and cutting it as it dried into cubes about 5 mm.

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[10] Davis, *Ind.* Eng. Chem., Anal. Ed., 1, 61 (1929).

on an edge. In order to insure that the filling did not contain moisture, the tube was heated to 500° along the filled length while a stream of dry nitrogen was passed through. The volume of the filling was determined after the run by pouring it into a graduated cylinder partly full of water and noting the volume increase. Before each experiment: the whole train was swept out with dry nitrogen.

The furnace used was thrown directly on the line and carried a practically constant current during the run. The temperatures were taken inside the tube at the end of the operation and, as can be seen from the table, varied from 890 to 900°. These correspond to a temperature outside the tube of 980".

Cyanide was tested for in the usual way by boiling an alkaline solution of the sample with ferrous sulfate and ferric chloride solutions, and then acidifying to obtain Prussian blue.

In Run No. 2, the only one made at 600°, 2 g. of acetonitrile, b. p. 79–80', was definitely identified.

In Run No. 4 cyanogen was tested for by passing the off gas through concentrated hydrochloric acid. No oxamide was obtained, as is the case when even traces of cyanogen are present."

Benzylamine.—Benzylamine from Eastman Kodak Company was used. In sealed tube experiments this material was recovered practically unchanged after five hours of heating at 275° and eight hours at 300°. In the latter experiment, however, a positive test for secondary amine was obtained by Liebermann's nitroso reaction. Using the flow method through a pyrex tube, benzylamine was also recovered unchanged at 535° with a contact time of fifty-four seconds.

Pyrolysis at 630°.—Fifteen grams of benzylamine was allowed to run very slowly during 8.25 hours from a dropping funnel into a 50-cc. distilling flask heated at 270° in a fused salt bath. The arm of the distilling flask was connected to an unfilled pyrex tube (1.1 X 60 cm.) heated to 630° in a gas combustion furnace. The thermocouple was encased by a small pyrex tube within the main reaction tube. The products were condensed in a 25-cc. distilling flask surrounded by an ice–salt bath. A U-tube, at the same temperature and in series with the first receiver, collected nothing. The system was swept out with nitrogen before the run.

A contact time of 160 seconds was used. From a 15-g. sample were obtained 13.1 g. of liquid product and about 1500 cc. of gas insoluble in water. Hydrogen cyanide and ammonia were also evolved. Distillation of the liquid product gave 20 g. of benzene boiling up to 90°; 2.28 g. at 90–103° (mostly at 102°) identified as toluene; 1.38 g. of a mixture of products at 103–185°. Continuation at 50 mm. gave 2.85 g. at 102°, identified as benzonitrile through evolution of ammonia and formation of benzoic acid on boiling with potassium hydroxide solution; at 102–190°, 0.90 g., one-third of which was identified as benzylamine. A dark mobile residue remained in the flask. Qualitative tests failed to show the presence of lophine or stilbene, which are listed as pyrolytic products[12] of di- and tribenzylamine.

The gas contained 81.5% hydrogen, 2.0% carbon monoxide, 6 0% saturated hydrocarbons (n in C_nH_{2n+2} = 1.22) and 10.5% nitrogen.

Pyrolysis at 700°.—A 30-g. sample of benzylamine was displaced by mercury from a graduated capsule into a vertical pyrex tube heated in a multiple unit electric furnace held at 700" by a Leeds and Northrup recording controller. The time was fifty-eight minutes, the tube 2.1 X 90 cm., giving thus a contact time of 49.4 sec. The bottom of the reaction tube was sealed to a piece of smaller bore. The latter extended into a 100-cc.

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[11] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1916, Vol. II, p. 226.

[12] Limpricht, *Ann.*, 144,307 (1867); Brunner, *ibid.*, 151, **133** (1869).

distilling flask immersed in an ice–salt bath. A U-tube in series with the first receiver and at the same temperature collected nothing. The residual gas was collected over water.

The weight of liquid product was 26.2 g. Distillation gave 4.3 g. of material boiling up to 110" at ordinary pressure. This distillate was evidently a mixture of benzene and toluene as previously encountered. Distillation of the residue at 23 mm. gave a product at 80–85° which weighed 18.1 g. While it possessed the characteristic odor of benzonitrile, it gave practically no benzoic acid on hydrolysis with potassium hydroxide. Treatment of 1.8 g. with 35 cc. of 2 N potassium hydroxide and 5.0 g. of *p*-toluenesulfonyl chloride gave 3.7 g. of *p*-toluenesulfonebenzylamide, corresponding to the yield from a pure sample. The derivative melted at 117° on recrystallization from methyl alcohol, and a mixed melting point with an authentic sample confirmed its identity.

Three liters of gas was collected which, by volume, was 68.8% hydrogen, 10.1% saturated hydrocarbons ($n = 1.09$). 11.3% nitrogen, 2.3% carbon monoxide, 4.4% oxygen and 0.1% carbon dioxide.

Preparation of *p*-Toluenesulfonebenzylamide.—A mixture of 5.4 g. of benzylamine, 18 g. of p-toluenesulfonyl chloride and 100 cc. of 2 N potassium hydroxide was allowed to stand overnight. After acidification of the mixture with 3 N hydrochloric acid, the solid material was filtered off. It was then boiled for five minutes with 75 cc. of 2 N potassium hydroxide, cooled and filtered. (A precipitate often forms here even when the hot alkali has given a clear solution; accordingly the separation must be applied with caution in the case of benzylamine mixtures. The treatment of alkali-insoluble material with sodium ethoxide should never be omitted. The solution was made by dissolving 0.4 g. of sodium in 10 cc. of 95% alcohol for each gram of base used. Under the conditions the primary amine derivative is soluble.) The filtrate was acidified with hydrochloric acid and the product filtered off.

The crude weight was 9 g., 69% of the calculated amount. Purification was effected by one or two crystallizations from methyl alcohol, using bone black. The pure product melted at 117.8' (119°, corr.).

Anal. Subs., 0.4478, 0.4101: 0.1311 N HCl, 13.06, 11.88. Calcd. for $C_{14}H_{15}O_2NS$: N, 5.36. Found: N, 5.34, 5.33.

Preparation of *p*-Toluenesulfonedibenzylamide.—*p*-Toluenesulfonedibenzylamide was also prepared for purposes of comparison. A mixture of 2 g. of benzylamine and 3 g. of benzyl bromide was allowed to stand for three hours. A crystalline hydrobromide separated. Without any preliminary separation, 40 cc. of 2 N potassium hydroxide solution and 6 g. of p-toluenesulfonylchloride were added. The mixture was allowed to stand overnight and was worked up in the usual way. The alkali-insoluble material was treated with sodium ethoxide. The residue from this operation was crystallized from methyl alcohol accompanied by treatment with charocoal. It formed small white needles, melting at 80.8° (81.3°, corr.).

Anal. Subs., 0.5526: 0.1311 *N* HCl, 12.06 cc. Calcd. for $C_{21}H_{21}O_2NS$: N, 3.99. Found: N, 4.01.

Summary

The subjection of ethylamine to a temperature of 600° has been found to produce largely acetonitrile and hydrogen. Some ethylene, ammonia, hydrogen cyanide and methane were also produced.

A number of pyrolyses of ethylamine at 890–900°, inside temperature, or 980° outside temperature, have been carried out with various tube

fillings and contact times. No butane was found in any instance although especial search was made for it because its presence has been inferred by other investigators. With a contact time of one second, the gas produced carried 10.3% ethylene; 15.5 seconds, 5.0%; eighty seconds, 0.5 per cent; with longer contact time, none at all. Hydrogen cyanide was always present at 890–900°, but only traces of ammonium cyanide or acetonitrile were noted except in a run made with a contact time of one second. In this particular run the saturated hydrocarbon content was also unusually high. Cyanogen is not a product of the pyrolysis.

Benzylamine was unchanged on being heated for several hours at 275–300° in a sealed tube. It was, furthermore, almost unchanged at 535° with a contact time of fifty-four seconds.

Benzylamine decomposed in 160 seconds at 630° to give benzonitrile, benzene, toluene, saturated hydrocarbons, hydrogen, hydrogen cyanide and traces of secondary amine. A mechanism for the reaction has been proposed.

p-Toluenesulfonebenzylamide and *p*-toluenesulfonedibenzylamide have been synthesized and characterized.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

RESEARCHES ON CHLORIMINES. II. SOME NEGATIVELY SUBSTITUTED AROMATIC ALD-CHLORIMINES

BY C. R. HAUSER, M. L. HAUSER AND A. GILLASPIE[1]

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A recent communication[2] from this Laboratory has described the preparation and properties of o-chlorobenzalchlorimine and anisalchlorimine. It has been shown that the latter compound undergoes spontaneous decomposition more rapidly than does the former, according to the general equation $RCH{=}NCl = RCN + HCl$. This difference in rate of decomposition of these compounds suggests that the nature of a substituent group in an aromatic ald-chlorimine may be an important factor in its stability.

In the present investigation a number of aromatic ald-chlorimines have been prepared with the purpose of studying the effect of the presence of substituent groups on the stability of these compounds as well as extending the list of readily available ald-chlorimines to be used in subse-

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[1] This paper is in part constructed from portions of a thesis presented by A. Gillaspie in partial fulfilment of the requirements for the degree of Master of Arts in the Graduate School of Arts and Sciences, Duke University.

[2] Hauser and Hauser, THIS JOURNAL, 52, 2050 (1930). It should be mentioned that Raschig seems to have condensed anisaldehyde with monochloramine but no details are given; Raschig, "Schwefel und Stickstoff-Studien," 1924, p. 80.

quent work. Excellent yields of certain chlorimines have been obtained within a few minutes by reaction of aldehydes in ethereal solution with monochloramine in cold aqueous solution. A comparison of the temperatures at which the purified chlorimines decomposed when heated gradually, and of the rates of decomposition at 30°, showed that certain ones were more stable than others, but since the decompositions are apparently catalyzed by impurities and reproducible results were not obtained in several cases, only a general classification of these compounds seems warranted at this time. In general, anisal-, o-methoxybenzal-, piperonal- and o-nitrobenzal-chlorimines comprise a relatively unstable class as compared with o-chloro-, *p*-chloro-, *p*-bromo- and 2-chloro-5-nitro-benzal-chlorimines.

Experimental

Preparation of Ald-chlorimines from Solid Aldehydes.—Although several ald-chlorimines have been prepared by using alcohol as solvent, they were generally best prepared when solid aldehydes were used by vigorously shaking an ether solution of the aldehyde with a cold aqueous solution of monochloramine. By this method all of the aldehydes studied, with the exception of one, were rapidly converted into the corresponding chlorimines in 80–90% yields. The exception was *p*-dimethylaminobenzaldehyde which, when allowed to react with monochloramine by the method described below, was recovered in great part unchanged. However, when alcohol was used as solvent a small amount of dark colored material, which appeared to consist of some unstable chlorimine, was obtained. This was not further studied in this investigation.

The following method was adopted for the preparation of the chlorimines from solid aldehydes. An ether solution[3] of the aldehyde was vigorously shaken with three times the calculated amount of freshly prepared cold alkaline monochloramine[4] solution (1 *N*) containing crushed ice. A milky mixture or emulsion was formed almost immediately, and usually within a minute or two a precipitate was produced. After shaking for several minutes or until the solid material had coagulated sufficiently, the product was filtered and washed thoroughly with cold water. A yield of more than 85% of crude chlorimine was usually obtained.

Recrystallization and Analysis.—The chlorimines were best recrystallized from either 95% alcohol or acetone in the following manner. The sample was dissolved at room temperature (18–24°), the solution filtered and cold water added to the mixture until the precipitate which formed at first just redissolved on shaking. On standing in a cool place the product crystallized out. It was immediately filtered, dried on a porous plate and analyzed for active chlorine. The method of analysis previously described[a] has been modified as follows. A sample of chlorimine weighing 0.15–0.20 g. is dissolved in approximately 50 cc. of 95% alcohol, cooled and 10 cc. of 10% potassium iodide solution added. The cooled solution is then acidified with 0.5 cc. of concentrated hydrochloric acid and standard sodium thiosulfate solution immediately run in until the color of the solution has become light yellow. Starch indicator is next added, and then sufficient water to produce the characteristic blue color, after which the titration with thiosulfate is completed. In cases where the sample is sparingly soluble in 95% alcohol,

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[3] The best results were obtained when 5–7 cc. of ether per 100 cc. of aqueous monochloramine solution was used.

[4] See Hauser, THIS JOURNAL, 52, 1108 (1930).

the analysis may be conveniently carried out in acetone solution or equally well in a mixture of the two solvents.

General Properties.—All of the chlorimines studied were obtained as crystalline compounds which underwent spontaneous decomposition yielding, as primary products, hydrogen chloride and the corresponding nitrile. When heated rapidly on a platinum foil or in a capillary tube they decomposed with a "puff" evolving a cloud of hydrogen chloride. The melting points and the decomposition temperatures of the chlorimines were determined, as soon as the compounds were dry, in the following manner. A capillary tube containing the sample was immersed in a bath which was 5–10° below the melting point of the substance, and the temperature raised at the rate of 1° in five to eight seconds. When the temperature of the bath was raised'above the melting point of the substance at about this rate, some of the compounds decomposed rather vigorously while in other cases the first evidence of decomposition was the appearance of a cloudiness and then a precipitate. Sometimes the melted compound frothed and rose in the tube before precipitating.

Attempts to isolate stereoisomers from products which had been melted and then solidified again, were unsuccessful. Fractional crystallization of crude chlorimines from alcohol or from hydrocarbon solvents yielded no isomers.

Piperonalchlorimine, obtained as white crystals from alcohol, melted at 68–69° and precipitated at **72–77'.** Sometimes the compound did not melt completely before precipitation began. On further heating more decomposition with discoloration resulted.

Anal. Calcd. for $CH_2O_2C_6H_3CH{=}NCl$: **Cl, 19.33;** N, **7.63.** Found: **Cl, 19.25, 19.20; N, 7.88.**

A sample **(0.3** g.) was immersed in a bath at **70–74'** until it melted and precipitated. It was then cooled and pressed on a plate, after which it melted at 58–65°. When mixed with some pure chlorimine the melting point was **63–67°. Recrystallization** of the material yielded pure chlorimine, m. p. **68–69'.** When **0.5** g. of chlorimine was immersed in a bath at 80°, it "puffed" vigorously, evolving hydrogen chloride, and **nitrile** was isolated from the residue. The **nitrile** was also isolated from a sample which had been allowed to decompose in a desiccator containing sodium hydroxide. **A** small amount of another substance, insoluble in ether, apparently the **imine** hydrochloride, was also obtained. **A** sample of chlorimine left on a plate for two hours at room temperature **(25–27°)** melted at **66–69°** and decomposed more readily than a **freshly** prepared product.

o-**Nitrobenzalchlorimine,** obtained as pale yellow crystals from alcohol, melted at **74–75"** and frothed at **84–85'. Since** the crude chlorimine soon darkens in color if allowed to remain in contact with the alkaline **monochloramine** solution, the product should be **filtered** as soon as it has coagulated.

Anal. Calcd. for $NO_2C_6H_4CH{=}NCl$: **Cl, 19.22.** Found: **Cl, 19.00.**

***m*-Nitrobenzalchlorimine** melted at **79–80'** and precipitated again at **81–83°.** Sometimes the compound did not melt completely, but merely softened and then began to solidify. **Its** crystals are white when pure, but usually they were slightly colored even after two crystallizations from alcohol.

Anal. Calcd. for $NO_2C_6H_4CH{=}NCl$: **Cl, 19.22.** Found: Cl, **19.15, 19.10.**

In one case the crude chlorimine after drying on a plate was dissolved in a small amount of benzene and filtered. When treated with about **4** volumes of **ligroin** a small **quantity** of light tan crystals was produced and filtered off. When the filtrate was cooled, white crystals were obtained. In a similar manner two crops of crystals were obtained from the crude chlorimine by using chloroform and ligroin. A **third** fraction was also obtained from the latter solvents by allowing them to evaporate spontaneously, until only a trace of the solvent remained. The crystals were then washed with a small amount of ligroin. The melting points of the various fractions ranged from 74 to 79°. By the mixed melting point method it was shown that all of the fractions were identical. A crude preparation of the chlorimine was also fractionally crystallized from alcohol and mixed melting points were taken with the crystals obtained from the other solvents mentioned above. All of the crystals were identical

When a sample of this chlorimine which had been allowed to decompose in a desiccator over sodium hydroxide was treated with ether, practically all of the material dissolved. The nitrile was isolated, but no appreciable amount of the imine hydrochloride was found.

This chlorimine was compared with its ortho isomer as follows. When samples of *m*- and o-chlorimines in capillary tubes were immersed together in a bath at 80°, and heated, they both melted. At 83–85" the meta compound solidified, and at 95" the ortho compound frothed and decomposed. When the two chlorimines were immersed at 117°, both melted, and after a few seconds the meta "puffed;" after a few more seconds the ortho compound did likewise.

_p_-Chlorobenzalchlorimine, obtained as small white needles from alcohol or acetone, melted at 79–80°, became slightly cloudy at 95" and boiled up and solidified at 115–120°. Several preparations of this chlorimine heated in the same manner gave the following average results: became slightly cloudy at 90–95°, frothed or boiled up and precipitated at 100–127°.

Anal. Calcd for $ClC_6H_4CH{=}NCl$: Cl, 20.39; N, 8.05. Found: Cl, 20.33, 20.10; N, 8 00, 8.19.

When the chlorimine was recrystallized from warm petroleum ether, needles were obtained which melted at 78–79", and precipitated at 95°. Some colorless rectangular needles 7–12 mm. long, obtained by the partial spontaneous evaporation of a chloroform–ligroin or benzene–ligroin solution at room temperature, melted at 79–80", became slightly cloudy at 90–95", and continued to decompose with increasing temperature until at 122" the compound boiled up and solidified.

Crude preparations of this chlorimine were fractionally crystallized from chloroform and ligroin and from alcohol and water. The first fractions comprised a small proportion of the material used. The last fraction from the alcohol was obtained by the addition of excess water as long as a precipitate was formed. By the mixed melting point method it was shown that all the fractions were identical.

_p_-Bromobenzalchlorimine, obtained as white crystals, melted at 87–88°, became slightly cloudy at 90–95° and precipitated at 95–103°. At 120° more decomposition occurred. The chlorimine melted when immersed in a bath at 100–105°, and then a precipitate formed which partly dissolved when agitated for several minutes. It was evident that the chlorimine slowly decomposed with the gradual evolution of hydrogen chloride.

Anal. Calcd. for $BrC_6H_4CH{=}NCl$: Cl, 16.24; N, 6.41. Found: Cl, 16.23; N, 6.67.

2-Chloro-5-nitrobenzalchlorimine melted at 85–86', frothed at 110°, and underwent more decomposition at 115°. Its crystals are white when pure.

Anal. Calcd. for $ClNO_2C_6H_3CH{=}NCl$: Cl, 16.20. Found: Cl, 16.25.

o-Methoxybenzalchlorimine, melted at 35–36° and frothed at 83–85". After standing for several hours on a porous plate at 18–20', it "puffed" mildly at 75°. This chlorimine precipitates with difficulty when the aldehyde is shaken with a solution of monochloramine according to the method[2] recently described for the preparation of anisalchlorimine. Two unsuccessful attempts were made before it was finally obtained as a white precipitate.

Anal. Calcd. for $CH_3OC_6H_4CH{=}NCl$: Cl, 20.92. Found: Cl, 20.70.

o-Chlorobenzalchlorimine has been obtained as a precipitate from Eastman's o-chlorobenzaldehyde (m. p. 8–9°) and monochloramine within three to five minutes when prepared according to the method[2] recently described, and within six to eight minutes when ether was used according to the method outlined in the present paper.

When this compound was heated gradually in a capillary tube, decomposition began at 110–118°. After this chlorimine had decomposed on standing in a desiccator over sodium hydroxide at 30°, the nitrile was isolated from the products. The material insoluble in ether or benzene consisted partly of ammonium chloride and of some unidentified substance.

Anisalchlorimine was prepared according to the method[3] recently described. When a sample was heated in a capillary tube it decomposed with a puff at 60–70°. One preparation of the crude chlorimine was fractionally crystallized from alcohol and water. Four fractions of about equal amounts were obtained. After drying it was shown by the mixed melting point method that all of the fractions were identical.

Stability of Chlorimines.—It has already been reported that anisalchlorimine is much less stable than o-chlorobenzalchlorimine. While working with the chlorimines described in this investigation, it soon became evident that certain ones were much more unstable than others. A qualitative classification of these compounds according to their stabilities was arrived at from a consideration of the temperatures at which the chlorimines decomposed when heated gradually in capillary tubes, and from a consideration of the length of time which they could be kept at room temperature without undergoing appreciable decomposition. Although anisalchlorimine appeared to be the least stable of any of the compounds described here, this compound along with o-methoxybenzal-, piperonal- and o-nitrobenzal-chlorimines, formed a class which was far more unstable than o-chloro-, *p*-chloro-, or *p*-bromo- and 2-chloro-5-nitrobenzalchlorimines. From a consideration of the temperature at which m-nitrobenzalchlorimine began to decompose, this compound should be classed with the unstable chlorimines. However, several preparations of the m-nitro compound were kept at room temperatures (18–24°) for several days without appreciable decomposition.

In an attempt to obtain a quantitative measure of the relative stabilities of these compounds, their velocity of decomposition was determined at 30°. After the chlorimines were purified by recrystallization from alcohol, and dried on a porous plate at room temperature (18–24°), weighed samples in small vials were placed in a desiccator which contained solid sodium hydroxide and kept in an air-bath at 30°. At suitable intervals the samples were analyzed for active chlorine. The data obtained are recorded graphically in Fig. 1.

It is evident from Fig. 1 that the qualitative classification of these compounds mentioned above is in general supported by these curves. While the rates of decomposition of the relatively unstable chlorimines checked fairly well, reproducible results were not obtained for some of the other compounds.

The product used in the determination of Curve 4 was prepared when the room temperature was about 20° and, after drying, an initial analysis of the compound was in close agreement with the theoretical. However, when the work was repeated the room temperature was about 30°, and although the compound was recrystallized several times from alcohol, analyses, after drying, gave low results, which indicated that some decomposition had occurred during the process of drying. This product decomposed at a much more rapid rate at 30° than that represented by Curve 4. After sixty-four hours the chlorimine was 20%, and after **110** hours, 47% decomposed. Similar results were obtained when crude m-nitrobenzalchlorimine was recrystallized from slightly warm chloroform and ligroin. These observations indicate that, in some cases at least, the rates of decomposition are catalyzed by the impurities present. A preliminary experiment showed that the rate of decomposition of m-nitrobenzalchlorimine was accelerated by *a* **nitrile** and retarded by **an** aldehyde.

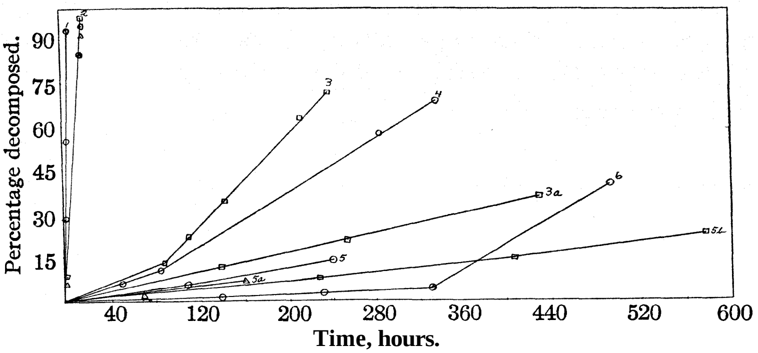

Fig. 1.—Rates of decomposition of ald-chlorimines at 30°. Curve 1, anisal- at 20–22°; o-methoxybenzal- gave approximately the same curve at 30°. Curve 2, points ○ and A, piperonal-; points □ and ⊗, *o*-nitrobenzal-. Curves 3 and 3a, o-chlorobenzal- (liq. at 30°). Curve 4, *m*-nitrobenzal-. Curves 5, 5a and 5b, *p*-chlorobenzal-. Curve 6, p-bromobenzal-.

Summary

A number of new aromatic ald-chlorimines have been prepared and their stabilities studied. In general, anisal-, o-methoxybenzal-, piperonal- and o-nitrobenzalchlorimines comprise a group which are distinctly less stable than o-chloro-, *p*-chloro-, p-bromo- and 2-chloro-5-nitrobenzalchlorimines.

DURHAM, NORTH CAROLINA

NOTES

The β-Chlorovinyl-arsines.[1]—The work of Miller and Witherspoon[2] has shown that the compound obtained by reacting β-chlorovinyl-dichloroarsine with diphenylamine is not 6-β-chlorovinyl-phenarsazine, as reported in the above entitled article, but 6-chloro-phenarsazine. The compound is extremely difficult to obtain pure by crystallizing from solvents. Five crystallizations from xylene gave a product melting at 189° (uncorr.). By vacuum sublimation, Miller reports a melting point of 193–194°.

Similar correction should hold for the product obtained when phenyl-α-naphthylamine is condensed with β-chlorovinyl-dichloro-arsine. Thus in both cases the amines apparently condense with arsenic chloride, present as a result of decomposition or equilibrium, giving a chloro-arsine and not a chlorovinyl-arsine.

W. LEE LEWIS
H. W. STIEGLER

RECEIVED JUNE 23, 1930
PUBLISHED OCTOBER 6, 1930

Preparation of Benzene-azo Derivatives of 8-Hydroxyquinoline.—According to J. Mathëus,[1] the alkaline coupling of 8-hydroxyquinoline with diazobenzene-chloride gives 5-benzene-azo-8-hydroxyquinoline. In the present work, which was executed to obtain such a compound for use in the Skraup reaction with certain azo compounds, when diazobenzene-chloride and 8-hydroxyquinoline were coupled in equimolecular proportion in an alkaline medium with as small an amount of water as possible, the chief product obtained was found to be 5,7-benzene-disazo-8-hydroxyquinoline, which after three recrystallizations from alcohol gave deep violet crystals of excellent purity; m. p. 205–206°; yield, 16 g. from 14.5 g. of 8-hydroxyquinoline. Its alcoholic solution assumes a red color, and the solution in concd. sulfuric acid is indigo blue, but on addition of alcohol the color changes to violet red.

Anal. Subs., 6.320: CO_2, 16.558; H_2O, 2.488. Subs., 3.115, 1.897: N_2, 0.576 cc. (30°, 762 mm.) 0.344 cc. (31°, 756 mm.). Calcd. for $C_{21}H_{15}ON_5$: C, 71.39; H, 4.25; N, 19.83. Found: C, 71.45; H, 4.37; N, 20.08, 19.41.

On the other hand, when the coupling was conducted in a very dilute solution, the mono-azo compound was the chief product, which after four recrystallizations from alcohol gave brownish-yellow needles (m. p. 185–186°); its properties were identical with those of 5-benzene-azo-8-hydroxyquinoline given by Mathëus. The mono-azo compound, however, was

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[1] "The β-Chlorovinyl-arsines and their Derivatives," W. Lee Lewis and H. W. Stiegler, THIS JOURNAL, 47,2546 (1925).

[2] Unpublished, Chemical Division, Edgewood Arsenal, Maryland.

[1] Mathëus, Ber., 21, 1644 (1888).

found to be readily obtained in a very pure state in almost the calculated quantity when the two components were coupled in an acetic acid medium, and after only one recrystallization from alcohol gave orange-yellow needles of m. p. 187°. Its yellow alcoholic solution, on the addition of ferric chloride, assumes a deep brown color and the solution in concd. sulfuric acid is red.

Anal. Subs., 4.372: CO_2, 11.558; H_2O, 1.875. Subs., 3.988: N_2, 0.578 cc. (21°, 760.4 mm.). Calcd. for $C_{15}H_{11}ON_3$: C, 7229; H, 4.42; N, 16.87. Found: C, 72.10; H, 4.77; N, 16.66.

The hydrochloride gave orange needles; m. p. 227° (decomp.). On pouring into water, it readily undergoes hydrolysis with the separation of the free base.

Anal. (Water of crystallization). Subs., 0.5407: H_2O, 0.0513. Calcd. for $C_{15}H_{12}ON_2Cl\cdot 1^1/_2H_2O$: H_2O, 9.05. Found: H_2O, 9.49. Subs., 0.2550: AgCl, 0.1321. Calcd. for $C_{15}H_{11}ON_2\cdot HCl$: HCl, 13.44. Found: HCl, 13.17.

Furthermore, the disazo compound could also be obtained by the alcoholic alkaline coupling of the mono-azo compound with diazobenzenechloride, but its quality was found to be far inferior after repeated recrystallizations from alcohol.

CONTRIBUTION PROM THE
CHEMICAL LABORATORY OF
KITASATO INSTITUTE
TOKYO, JAPAN
KONOMU MATSUMURA

RECEIVED JUNE 2, 1930
PUBLISHED OCTOBER 6, 1930

The Direct Nitration of Furfural.—In continuation of studies concerned with substitution reactions of sensitive furan types,[1] it was found possible to prepare 5-chloro-2-furfural by chlorination not only of furfural diacetate but also of furfural. This suggested that it might be possible to nitrate furfural directly, and so avoid the prior, independent preparation of furfural diacetate. Experiments have confirmed this expectation.

Using the same molar proportions and technique described previously, the yield of nitrofurfural *diacetate* obtained from 96 g. (1 mole) of freshly distilled furfural was 110 g., or 45%, melting at 85°. When crystallized from hot alcohol, the yield of pure nitrofurfural diacetate melting at 92° was 80 g., or 33%.

In the treatment with alkali subsequent to nitration of the furfural, sufficient sodium hydroxide is added to the iced mixture to give a faint but distinct alkaline reaction to litmus. The oil obtained in this manner is separated by decantation from the aqueous solution, and then warmed with sufficient pyridine (not less than 250 cc.) to effect complete solution. The

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[1] Gilman and Wright, THIS JOURNAL, 52, 2550 (1930); see also, Gilman and Wright, *ibid.*, 52, 1170 (1930).

acetic acid removed in this manner from the intermediate compound, which may or may not be a product of ring scission, can also be removed by means of other bases like dimethylaniline. The nitrofurfural is readily obtained, if necessary, by hydrolysis[1] of the crude diacetate.

The authors are grateful to Mr. A. P. Hewlett for assistance.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
IOWA STATE COLLEGE
AMES, IOWA

HENRY GILMAN
G. F. WRIGHT

RECEIVED JUNE 24, 1930
PUBLISHED OCTOBER 6, 1930

A Note on the Preparation of Glycine.—The classical method of preparing glycine through the interaction of chloro-acetic acid and ammonia with the subsequent formation of the copper or lead salt has been abandoned by Clarke and Taylor[1] in favor of a method involving the hydrolysis of methylene-amino-acetonitrile. The starting material is fairly expensive and the yield of 31–37% is not high. Robertson,[2] after a study of the velocity and course of the reaction between chloro-acetic acid and ammonia, recommends the use of a large excess of ammonia. When the molecular ratio of ammonia to chloro-acetic acid is 60:1, the actual concentration of glycine in solution is increased to 86%. He eliminates the ammonium chloride by means of silver oxide and obtains a final yield of 50% of pure glycine.

It was thought that a correspondingly large yield of pure glycine could be obtained by making use of this high ratio of ammonia to chloro-acetic acid, and crystallizing the glycine directly from the concentrated reaction mixture in the presence of pyridine according to the method of Clarke and Taylor or in the presence of aniline as suggested by Benedict,[3] thus eliminating the time and expense involved in the use of silver oxide to remove the ammonium chloride. The attempt proved successful and the following method was worked out.

Two moles of chloro-acetic acid (189 g.) is dissolved in 8 liters of ammonium hydroxide (sp. gr. 0.90) in a 12-liter flask and allowed to stand at room temperature for forty-eight hours. The excess of ammonia is distilled off and recovered. The mixture is concentrated, in *vacuo* if preferred, until precipitation of ammonium chloride begins. The salt is dissolved by warming on the steam-bath with the addition of the smallest possible volume of water. If the solution is not clear, it is filtered by suction. The filtrate and washings should occupy a volume of about 500 cc. A

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[1] Clarke and Taylor, "Organic Syntheses," John Wiley and Sons, Inc., New York. 1925, Vol. IV, p. 31.

[2] Robertson, THIS JOURNAL, 49, 2889 (1927).

[3] Benedict, *ibid.*, 51, 2277 (1929).

mixture of 800 cc. of methyl alcohol and 140 cc. of pyridine is stirred in. Crystallization of the glycine begins at once. After standing overnight, the glycine is filtered off, suspended in methyl alcohol, filtered and washed with methyl alcohol. A yield of 96 g. or 64% is obtained. A further yield of 2 to 3 g. may be secured from the combined mother liquor and washings on standing. If an attempt is made to crystallize the glycine from a warm solution of much greater concentration than the one suggested, the product will be contaminated with considerable ammonium chloride. This may be almost completely removed by washing with methyl alcohol. The glycine is recrystallized by dissolving in 300 cc. of water with warming. In order to remove the last traces of ammonia, 6 g. of permutit is added and after thorough stirring the mixture is filtered through a charcoal mat. The solution with washings should occupy about 400 cc. and should be crystal clear; 800 cc. of methyl alcohol is stirred in and the mixture is allowed to stand overnight until crystallization is complete. The glycine is filtered off and washed with methyl alcohol. The yield is 81 g. or 54%. The product is free from the chloride ion and from ammonia, as shown by testing with Nessler solution. It melts at from 225–230° (corr.), and shows the theoretical percentage of nitrogen and amino nitrogen. An equivalent amount of aniline may be substituted for the pyridine if desired in the first crystallization but the product carries a slight yellow color. This is completely removed on recrystallization.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
BELOIT COLLEGE
BELOIT, WISCONSIN

PAUL W. BOUTWELL
LEO F. KUICK

RECEIVED JUNE 30, 1930
PUBLISHED OCTOBER 6, 1930

***o*-Phenetylurea.**—On account of its industrial importance, dulcin has received considerable attention while the corresponding ortho derivative has been slighted. The writer finds but one literature reference in a paper by Pierron,[1] who prepared this compound from o-ethoxyphenylcyanamine as a means of identification of the latter. He quotes a melting point of 206°, which appears to be too high. It seemed worth while to make the compound principally in order to compare its properties with those of dulcin derivatives now in preparation.

A 5-g. portion of o-phenetidine is treated with 40 cc. of water and 2.5 cc. of concentrated hydrochloric acid. A solution of 2.25 g. of potassium cyanate in 20 cc. of water is added in small portions with a thorough shaking between additions. Precipitation is complete in about ten minutes. After filtration the solid is washed with dilute ammonium hydroxide and then with ether. It is at once recrystallized from hot dilute ethanol to

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[1] Pierron, *Ann chim. phys.*, [7] **15**, 145 (1908).

which sufficient ammonium hydroxide is added to give a decided odor. The crystals are washed with ether. When dry the purification is completed by a recrystallization from hot benzene; yield, 2 g.; white microscopic needles. The compound shows a slight shrinkage at about 139° and melts at 142–143°. It is tasteless and odorless. Concentrated sulfuric acid gives a colorless solution which upon heating becomes a faint straw color.

Anal. Calcd. for $C_9H_{12}O_2N_2$: C, 60.0; H, 6.66; N, 15.56. Found: C, 60.10; H, 6.72; N, 15.64.

The compound is soluble in hot water, ethanol, amyl alcohol and hot benzene. It is very slightly soluble in ether.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF THE
UNIVERSITY OF ARKANSAS
FAYETTEVILLE, ARKANSAS
E. WERTHEIM

RECEIVED AUGUST 23, 1930
PUBLISHED OCTOBER 6, 1930

COMMUNICATIATIOMS TO THE EDITOR

DR. C. S. HUDSON'S VIEWS ON THE RELATIONSHIP OF STRUCTURE TO THE OPTICAL ROTATIONS OF SUGARS

Sir:

Dr. C. S. Hudson has not utilized the means which were open to him to test the validity of his views by direct chemical experiments. The basis on which he develops his argument is the presumed existence, which his statistical methods enable him to detect, of a new form of mannose (calculated $[\alpha]_D$ +77°) in derivatives of 4-glucosido-mannose, obtainable from cellobiose through cellobial. If this foundation for his scheme fails, then the entire superstructure of rival formulas which he has raised upon it must collapse.

A survey of his two recent papers [THIS JOURNAL, 52, 1680, 1707 (1930)] has led me to select for this critical test an experimental method which he has tacitly approved: he has accepted and utilized the observation of Fischer and Armstrong that β-methylmaltoside gives rise by enzyme hydrolysis to β-methylglucoside without ring change. Implicit in Dr. Hudson's scheme, therefore, is the expectation that 4-glucosido-a-methylmannoside will yield by enzyme cleavage his hypothetical a-methylmannoside ($[\alpha]_D$ +125°), inasmuch as this is the glycoside of the unknown form of mannose to which he has assigned the 1,5-ring.

With my colleague Dr. E. L. Hirst and other co-workers (R. J. W. Reynolds, H. R. L. Streight, H. A. Thomas, J. I. Webb and Miss M. Plant) I have prepared and investigated the chemical behavior of both 4-glucosido-a-methylmannoside and 4-galactosido-a-methylmannoside to which the 1,4-ring cannot apply since the 4-position in the mannose residue is occupied by the biose link. Both these substances are hydrolyzed by *emulsin* and yield the ordinary known form of a-methylmannoside ($[\alpha]_D$ +79°) which is the pyranoside (1,5-ring).

The above biosides are prepared in the same way as the bioses, namely, from cellobial and lactal by the action of perbenzoic acid, but in the presence of methyl alcohol instead of water. The same 4-glucosido-α-methylmannoside has also been obtained from acetobromo-glucosido-mannose.

Had Dr. Hudson tried these experiments it is difficult to see how he could have committed himself to speculations that are at variance with this and with much more chemical evidence which is on record. Moreover, the rotations of these biosides and of the corresponding bioses are widely divergent from those required by his system of classification based on epimeric differences with cellobiosides and lactosides and the free sugars. The "principle of optical superposition" cannot be applied uniformly throughout the sugar group. The results now summarized are in complete agreement with the sugar formulas we have established by methylation studies, lactone formation and degradation, and by a comparison of the reaction velocities of glycosides under hydrolysis, and by other direct chemical methods.

THE UNIVERSITY OF BIRMINGHAM W. N. HAWORTH
EDGBASTON, ENGLAND
RECEIVED JULY 30, 1930
PUBLISHED OCTOBER 6, 1930

POSSIBLE USE OF THE POULSEN ARC AS A MEANS OF DETECTING TRACES OF IMPURITIES IN METALS

Sir:

It has been shown by one of us in conjunction with E. Z. Stowell[1] that an atmosphere of hydrogen and usually cathode materials which are elements of even atomic number are necessary to produce radio frequency oscillations in the Poulsen Arc.

In the non-oscillating or ordinary direct current arc in hydrogen, the spectra of copper and sodium were revealed when these elements were used as cathodes. Upon connecting the oscillating circuit, the spectra of copper or sodium were either entirely suppressed, or appeared only faintly. Simultaneously the spectra of elements such as zinc, titanium and aluminum which will support oscillation, and which were present in small amount as impurities in the cathode metal, either appeared or if previously present were greatly accentuated.

The spectrum of H_B showed the presence of more atomic hydrogen in the oscillating than in the non-oscillating arc. Chemical analysis of the electrolytic copper showed titanium and aluminum present as 0.005 and 0.0045%, respectively.

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[1] Stowell and Redeker, *Phys. Rev.*, **34**, 978 **(1929).**

When using an ammonia atmosphere and a tip of gold brazed onto a water-cooled copper cathode, the oscillating arc completely suppressed the spectra of these metals, and intensified the 3361–3372 Å. line of the titanium impurity in the copper. The above phenomena suggested the use of the Poulsen Arc as a means of detecting small traces of impurities of even atomic number in such metals as copper, gold and silver.

A quantitative analytical method involving these phenomena is now being worked out in this Laboratory.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIFORNIA
HARRY E. REDEKER
PHILIP A. LEIGHTON

RECEIVED SEPTEMBER 2, 1930
PUBLISHED OCTOBER 6, 1930

COAGULATION OF PURE FERRIC HYDROXIDE SOLS

Sir:

In a recent article Judd and Sorum [THIS JOURNAL, 52, 2598 (1930)] have stated that with highly purified sols of ferric hydroxide, which are practically free from chloride ions, the amount of univalent coagulating ion decreases as the concentration of the sol increases.

In several publications [J. Phys. *Chem.*, 26, 701 (1922); 28, 313 (1924); 29,435,659 (1925); *Kolloid.-Z.*, 34,262 (1924); 36, 129 (1925)] from these Laboratories we have shown that ordinarily purified sols of ferric hydroxide require larger amounts of univalent electrolytes for coagulation when the concentration of the sol is increased. In a recent communication Dhar and Gore [J. *Indian Chem. Soc.*, 6, 31 (1929)] have shown that even highly purified sols of ferric hydroxide containing a very small amounts of chloride ion follow the general rule that the greater the concentration of the sol, the greater is the amount of electrolyte necessary for coagulation irrespective of the valency of the coagulating ion. It appears, therefore, that the results of Judd and Sorum are not in agreement with previous work and need confirmation.

CHEMICAL LABORATORY
ALLAHABAD UNIVERSITY
ALLAHABAD, INDIA
N. R. DHAR

RECEIVED SEPTEMBER 6, 1930
PUBLISHED OCTOBER 6, 1930

A CONTINUOUS (OR BAND) FLUORESCENCE EMISSION SPECTRUM WHICH ACCOMPANIES A CHANGE OF COLOR

Sir:

An interesting phenomenon has been observed in a study of the Raman effect with a number of liquids listed later. A continuous (or band) emission spectrum (Fig. 1) has been found to appear on the plate in each case in which the colorless liquid becomes colored, and not to appear if there is no color change. The incident radiation of the mercury arc light appears to excite the molecules of the substance, and a part of the energy of excitation is released as a fluorescence radiation. A few of the details of this work are given below.

The Raman effect has been observed for a number of bromides: normal butyl bromide, secondary butyl bromide, isobutyl bromide, tertiary butyl bromide, normal propyl bromide, isopropyl bromide, normal amyl bromide and isoamyl bromide. The liquids were purified by distillation.

In addition to the lines of modified wave length, a continuous spectrum, which lies within the limits $\lambda = 4000$ Å. and $\lambda = 5500$ Å., was obtained with each liquid. The continuous spectrum was always accompanied by the appearance of a yellow color in the liquid. Usually an exposure of forty-eight hours sufficed for the production of the continuous spectrum; this, however, was not the case with n-propyl bromide, n-butyl bromide and secondary butyl bromide, since none of these showed either a continuous spectrum or a discoloration after being exposed to the mercury arc for forty-eight hours. If the time of exposure was extended to seventy-two hours or more, the continuous spectrum and the color change were observed for each of these liquids. In all cases where the exposure was long enough to give an intense continuous spectrum, the latter contained two regions of maximum intensity, one lying between the mercury lines at $\lambda = 4358$ Å. and $\lambda = 4916$ Å., and the other between the lines at $\lambda = 5460$ Å. and $\lambda = 5769$ Å.

Methyl and ethyl alcohols saturated with ammonia were studied for Raman spectra. The solutions were exposed to the mercury arc for ten to twelve hours. Methyl alcohol saturated with ammonia gave a continuous spectrum which was similar to that of the bromides in character and in position; the solution turned yellow during the exposure. Ethyl alcohol saturated with ammonia did not give a continuous spectrum or a color change. Neither of these two accompanying phenomena was observed in the case of the pure alcohols.

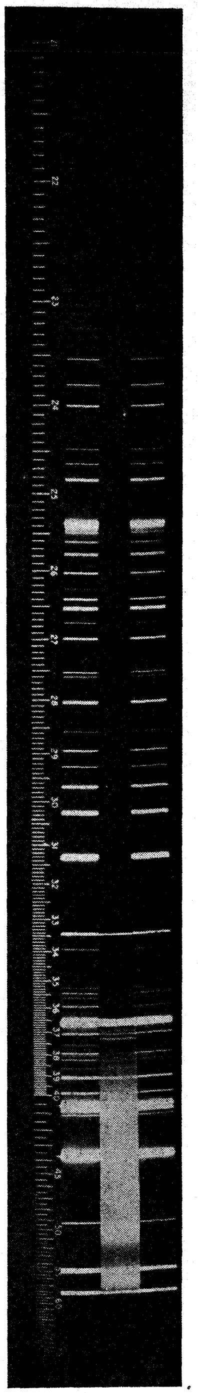


Fig. 1.—In the middle is the continuous fluorescence spectrum and the Raman spectrum of an alkyl bromide. The mercury comparison spectrum is shown above and below.

An attempt was made to ascertain whether the exclusion of oxygen would affect the color change and the continuous spectrum. A brisk stream of nitrogen was bubbled through isoamyl bromide for forty-five minutes prior to exposure and the Raman tube was closed by means of a stopcock; no diminution of the intensity of the continuous spectrum or of the color, was found.

KENT CHEMICAL LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

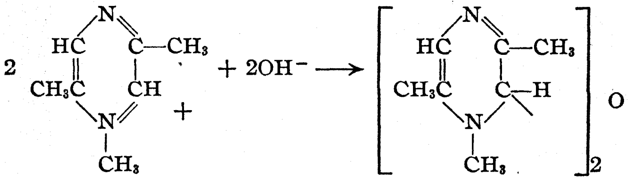
WILLIAM D. HARKINS
H. E. BOWERS

RECEIVED SEPTEMBER 8, 1930
PUBLISHED OCTOBER 6, 1930

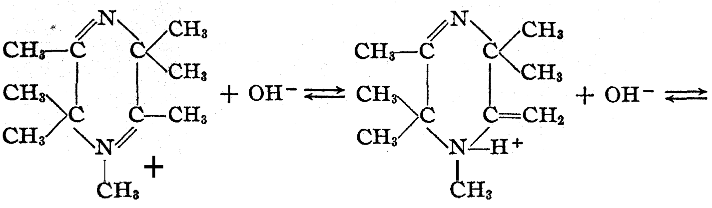
THE BASE FROM 2,5-DIMETHYLPYRAZINE-METHYL IODIDE

Sir:

Recently Princivalle[1] has reported unsuccessful attempts to isolate the base liberated from 2,5-dimethylpyrazine-methyl iodide. In connection with some work on pseudo bases, part of which has already been submitted for publication, the author has studied the action of alkali on this salt. Although the base isolated could not be obtained pure and gave analyses varying from C, 53.2; H, 6.94, to C, 49.5; H, 6.63, a kinetic study of the reaction using a conductimetric method has made it seem probable that the net reaction taking place is



The salts 1,2,2,5,5-pentamethyl-2,5-dihydropyrazinium iodide and 1,2,2,3,5,5,6-heptamethyl-2,5-dihydropyrazinium iodide have also been prepared and their behavior with aqueous alkali studied. From these two salts the bases isolated were, respectively, 1,2,2,5,5-pentamethyl-6-hydroxy-1,2,5,6-tetrahydropyrazine (m. p. 110°) and 1,2,2,3,5,5-hexamethyl-6-methylene-1,2,5,6-tetrahydropyrazine (b. p. (6.5 mm.) 78°). Certain evidence has been obtained to show that the latter base was formed by an enolic change



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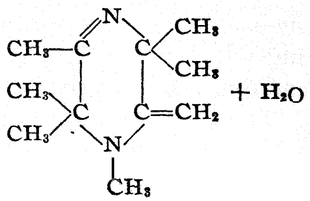
[1] Princivalle, *Gazz. chim. ital.*, 60, 298–301 (1930); *C. A.*, 24, 3792 (1930).



It is believed that the reduced conjugation in the ring is the cause of this reaction, which does not occur in the case of 1,2,5-trimethylpyrazinium iodide. It is to be noted that the same reduced conjugation occurs in 1,2,5-trimethyl-6-keto-1,6-dihydropyrazine-methyl iodide, which by the action of alkali yields 1,2,4-trimethyl-5-methylene-6-keto-1,6,4,5-tetrahydropyrazine.[2]

It seems likely, in view of the above results, that the last compound is yielded by an enolic change similar to that already mentioned and that the reduced conjugation is the important factor in its production.

DEPARTMENT OF CHEMISTRY
PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA
JOHN G. ASTON

RECEIVED SEPTEMBER 11, 1930
PUBLISHED OCTOBER 6, 1930

PRELIMINARY NOTE RELATING TO STUDIES ON KRYPTON AND XENON

Sir:

A research project having to do with the purification and properties of krypton and xenon has been in progress during the past four years. Some rather novel results have been obtained to which the authors desire to call attention at this time since the work has been interrupted on account of unavoidable delays attendant upon moving into a new building. A more complete report will follow at an early date.

Liquid air residues, mainly oxygen, were treated by cooled charcoal in a manner which concentrated the krypton and xenon considerably. The excess oxygen and other reactive gases were removed by suitable reagents and the remaining inert gases were separated by repeated fractional distillation. Finally about 70 cc. of krypton and 30 cc. of xenon were obtained in a condition of very high purity.

One of the first things investigated was the melting point. Krypton gave an exceedingly sharp melting point at $-156.6°$ with a corresponding vapor pressure of 558 mm. Note a difference of about 12° from the $-169°$ previously accepted as the melting point.

Xenon was harder to deal with in that it failed to give the sharp melting point that had been noted with krypton. Its behavior indicated the possibility of a transition point quite close to the melting point. The

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[2] Gastaldi and Princivalle, *Gazz. chim ital.*, 59, 791 (1929); Princivalle, *ibid.*, 60,296,298 (1930).

melting point may be given, however, as −111.5 ± 0.5° with a corresponding vapor pressure of 600 * 20 mm. The accepted value for the xenon melting point is approximately −140°.

The processes of purification were checked by frequent density determinations and the densities of the best samples of krypton and xenon were rather carefully determined. The method employed was to collect a sample of the gas at a known temperature and pressure in a calibrated bulb, which was then weighed against a counterpoised bulb.

Density determinations made in connection with the fractionation work seem to indicate that the present accepted densities for krypton and xenon are too low. The value found for the heaviest krypton fraction was **3.733** g./l. and that for the heaviest xenon fraction 5.887 g./l. These figures would correspond, respectively, to atomic weights of 83.6 and 131.4 if Watson's [J. *Chem. Soc.*, 97, 833 (1910)] corrections are employed. No effort has yet been made to make final density determinations and these will be reported later.

Much of the work of extraction and purification followed the lines indicated by earlier investigators, but a number of new methods were used which will be reported in the more complete paper.

CHEMICAL LABORATORY OF PURDUE UNIVERSITY
WEST LAFAYETTE, INDIANA
F. J. ALLEN
R. B. MOORE

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NEW BOOKS

Optical Activity and High Temperature Measurements. By F. M. JAEGER. McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York, 1930. 450 pp. 137 figs. 15.5 × 23.5 cm. Price, $4.00.

This volume contains the lectures delivered at Cornell University by Professor F. M. Jaeger during the second semester of 1928–1929 under the George Fisher Baker Non-Resident Lectureship in Chemistry. There are three series of the lectures. The first deals with the spatial arrangement of atomic systems and optical activity; the second with the methods, results and problems of precise measurements at high temperatures; the third with the constitution and structure of the ultramarines. Taken as a whole the lectures furnish a systematic presentation of investigations carried out by Professor Jaeger and his co-workers at the chemical laboratory of the University of Groningen.

The first lectures of the first series cover the principles of symmetry as applied to atomic systems, discussing the work of Pasteur, van't Hoff and Le Bel. The remaining lectures of this series are concerned chiefly with the optical activity of complex salts, many of them essentially inorganic. These latter lectures-are of particular interest as demonstrating the wide-spread occurrence of optical activity in the absence of any asymmetric carbon atom.

The lectures of the second series not only discuss and describe highly refined measurements of temperatures but also of specific heats and of the viscosities and surface tensions of liquids at elevated temperatures.

Systematic and connected accounts of this sort are always intrinsically useful, but this is particularly the case here, where the individual articles have already been published for the most part only in foreign journals.

We cannot but be grateful to Professor Jaeger and to the Baker Lectureship at Cornell for making it easy for us to become acquainted with these interesting and important researches.

ARTHUR B. LAMB

Physikalisch-chemische Übungen. (Manual of Physical Chemistry.) By W. A. ROTH, Professor in the Technical High School of Braunschweig. Fourth revised and enlarged edition. Leopold Voss, Leipzig, Germany, 1928. viii + 316 pp. 71 figs. 14 × 22.5 cm. Price, unbound, M. 13; bound, M. 15.

This fourth edition represents an extensive revision of this well-known manual, and is of interest as typifying the course in physical chemistry as given in the Technische Hochschule at Braunschweig. The manual is designed both for the beginners' course in which thirty obligatory exercises covering the general field are assigned, as well as for a more specialized course having an elastic program suitable as training for research candidates. The book is devoted largely to presenting the theory of the experiments and of the apparatus to be used along with concrete illustrative numerical examples.

Detailed directions for carrying out the experiments are exceedingly meager. Perhaps this is desirable. Instructive methods for evaluating graphically the errors in thermochemical experiments are set forth in considerable detail (pp. 72–75); likewise the introduction of nomographic methods deserves favorable comment, as well as the inclusion of experiments on the dielectric constant.

The treatment of electromotive force will be disappointing to most American readers. The reaction $Tl + KCNS \rightleftarrows TlCNS + KCl$ in aqueous solution with its uncertain and unavoidable liquid junction potential is certainly not a "htibsches Beispiel" today, particularly in discussing the Nernst Heat Theorem. The solubility of silver acetate in silver nitrate is discussed in detail in terms of the now obsolete degrees of dissociation of the salts followed by the statement (p. 159) "the small drift in solubility product becomes somewhat smaller on using activity coefficients," which makes one wonder if the "Moderne Anschauung" to which the student is referred has been grasped (*cf.* p. 157). The apparatus described for the conductivity experiments is hardly modern in character.

VICTOR K. LA MER

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. X. Sulphur and Selenium. By J. W. Mellor, D.Sc. Longmans, Green and Company, 55 Fifth Avenue, New York, 1930. x + 958 pp. 217 figs. 25 X 16 cm. Price, 520.00.

The present volume (Vol. X) of the Treatise represents a significant milestone in this great undertaking, for with it all the non-metals have now been covered. There remain still to be done the metals of Groups VII and VIII of the periodic system. Of these, iron in particular will require extended treatment.

This volume, like its predecessors, will be for the general reader as well as for students of inorganic chemistry an exhaustive and yet practical reference handbook.

ARTHUR B. LAMB

Die Anwendung der **Interferometrie** in Wissenschaft **und** Technik. (Applications of Interferometry in Science and Industry.) By E. BERL AND L. RANIS, of the Chemicotechnical and Electrochemical Institute of the Technical High School of Darmstadt. Gebrüder Borntraeger, W 35 Schoneberger Ufer 12 a, Berlin, Germany, 1928. v + 52 pp. 28 figs. 16.5 X 25 cm. Price, M. 5.20.

The intent of the authors is made clear in the preface of this booklet. The increasing number of applications of the interferometer to scientific and technical investigations justifies the special consideration of procedures and principles already described in the literature as well as additional new titration methods developed by the authors. Some of the topics discussed include (a) methods of measurement by the interferometer; (b) principle and construction of interferometers and their four general topics.

I. The gas interferometer.
    a Innovations in construction.
    b Calibration.
    c Calculations.
    d Absolute and relative calibration.
    e Selection of gases for comparison.
II. Possible application of the gas interferometer.
III. Interferometer for liquids.
IV. Field of application of the interferometer for liquids.

The special uses for these two types of interferometers described in the text are not given in detail. The reader is referred to original articles which are listed in each case. An exception to this is the application of the interferometer for liquids to various titrations. This is the special contribution of the authors and the description of this investigation constitutes one-half of the paper. The titrations include precipitation as well as neutralization reactions. Graphic representation of the data makes it possible to see at a glance the relative change of refractive index as the equivalence point of the titration is approached. From the many interesting examples given it is evident that the sensitivity of the interferometer makes possible the extension of the usual methods employed in Refractometry. The authors for the most part have given an applied rather than a highly theoretical presentation of the subject, The publication should prove to be interesting reading to those interested in technical and scientific applications of instrumental analysis.

VILLIERS W. MELOCHE

Select Methods of Metallurgical Analysis. By WILLIAM ARCHIBALD NAISH, Ph.D. (Eng.), A.R.S.M., B.Sc., P.I.C., M. Inst. M. M., and JOHN EDWARD CLENNELL, B.Sc. (London), Assoc. Inst. M. M. Introduction by Sir H. C. Harold Carpenter, F.R.S. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, 1930. xii + 495 pp. 32 figs. 15.5 × 24.5 cm. Price, $7.50.

In this book of five hundred pages a serious attempt has been made to give in concise form methods for the determination of all of the elements and analyses of most of the raw materials and products with which the metallurgical laboratory is confronted. The authors have taken up the elements alphabetically, giving selected and proved methods for their determination. In addition, methods are given for the complete analysis of ores and many metallurgical products, both ferrous and non-ferrous and including silicate analysis and fire assaying. Of course, it would not be possible within the scope of any ordinary sized book to take up in detail the complete analysis of all metallurgical materials, but the book is sufficiently complete to enable any reasonably trained metallurgical chemist to make chemical analysis of practically any metallurgical material. The book is so complete that it suffers somewhat from too great a condensation when giving analytical procedures. The chapter on "Electrometric Titration" is so condensed that it might almost as well have been left out, especially since the book does not make use of electrometric methods when describing the analytical methods used for each element. Perhaps the most outstanding omission in the book is its complete failure to include methods of gas analysis and its very sketchy two and one-half pages given to coal analysis. Neither is any mention made of water analysis.

From the point of pedagogy the chief criticism which the teacher of metallurgy will make will be directed against the almost complete absence of any discussion of the laws of physical chemistry as applied to the equilibria involved in the analytical procedures. This would be a serious matter if it were not for the fact that the teacher will have to drill the students in these matters anyhow. On the other hand, the authors are to be complimented on their thorough and uncompromising effort to give the chemical facts involved in analytical separations. There is all too great a tendency to neglect the facts and deal too much in theory in present-day pedagogy and book writing.

The most notable advance taken in this book is its up-to-date treatment of the application of spectrum analysis to the work of the metallurgical laboratory, because it is certainly true that metallurgists and metallurgical chemists must become "spectrum conscious." Since physical methods of analysis have been introduced in this chapter it would seem that the authors should have gone further and have included microscopic methods of analysis. The book is very thorough in its bibliography work, which will enable the users of it to get easily the details of procedure which the authors have been forced to omit.

This work will be frequently used in the reviewer's laboratory and will surely find a wide usefulness in the metallurgical world.

D. J. DEMOREST

Soap Films. A Study of Molecular Individuality. By A. S. C. LAWRENCE. **Foreword by Sir William Bragg, F.R.S. *G.* Bell and** Sons, **Ltd., Portugal** St., **London,** W. C. 2, England, 1929. xi + **141 pp. 61 figs. 14 × 22.5 cm. Price, 12s. 6d. net.**

Everyone interested in the intriguing subject of soap films—and everyone who dips into the pages of this unusual little book will find he is fascinated by it—will be under a debt of gratitude to Mr. A. S. C. Lawrence for having brought together in such readable form so much material of high scientific value which is not available elsewhere.

It is only those who have had the privilege of attending in person the Discourses at the Royal Institution, who will fully appreciate the opening sentence of Sir William Bragg's Introduction: "The researches of the late Sir James Dewar on the properties of soap films are well known for their variety, beauty and importance." The unrivaled practical experience in the demonstration of the properties of soap films and the production of black bubbles accumulated there through the course of many years was supplemented by the repetition of the more important studies of other investigators. The whole is vividly described and carefully discussed and systematized by the author, who was Lecture and Research Assistant to Sir James Dewar. The co-relation of these phenomena and the attempt to link them with existing theory represents, in itself, a substantial advance in this subject and will undoubtedly lead to further rapid developments. Amongst the subjects treated are discussions of surface tension and its inadequacy to explain the phenomena of soap films, reflection and interference of light by films, constitution of soap solutions and their surfaces and the remarkable phenomena presented by black and stratified films.

JAMES W. MCBAIN

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

PROPERTIES OF DIPHENYLAMINE AND DIPHENYLBENZIDINE AS OXIDATION–REDUCTION INDICATORS

BY I. M. KOLTHOFF AND L. A. SARVER

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Introduction

Knop[1] was the first to propose the use of diphenylamine as an indicator in the titration of ferrous iron by potassium dichromate, whereas Cone and Cady[2] recommended either diphenylamine or diphenylbenzidine as internal indicators in the titration of zinc by ferrocyanide. Several workers[3] have since shown that these indicators are reliable and useful in oxidation–reduction titrations, but Sarver[4] pointed out that end-points are often passed without any color formation, whereupon the addition of a trace of ferrous iron will then produce it instantly. Moreover, Watson[6] has recently shown that mercuric chloride has a powerful inhibiting effect on the color production.

Since diphenylamine and diphenylbenzidine now belong among the common analytical laboratory indicators it appeared desirable to make an extensive study of their properties in order to know in what cases they can be applied, under what conditions they give reliable results, and what corrections must be made under different circumstances. The physico-chemical part of this investigation will be presented here, while the analytical significance of the work will be reserved for a future paper.

I. Speed of Color Development.—Pure products of diphenylamine (m. p. 52–53', uncorr.) and diphenylbenzidine (m. p. 242–243°, uncorr.) have been used throughout this work, stock solutions being prepared by dissolving 0.1 g. of the substance in 100 cc. of concentrated sulfuric acid.

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[1] J. Knop, THIS JOURNAL, 46, 263 (1924).

[2] W. H. Cone and L. C. Cady, *ibid.*, 49, 356 (1927).

[3] W. W. Scott, *ibid.*, 46, 1396 (1924); N. H. Furman, *Ind. Eng. Chem.*, *17*, 314 (1925); J. P. Mehlig, *J. Chem. Ed.*, 3, *824* (1926); I. M. Kolthoff, *Rec. trav. chim.*, *45*, 745 (1926); *Chem. Weekblad*, 24, 203 (1927); H. H. Willard and P. Young, *Ind. Eng. Chem.*, 20, 764 (1928).

[4] L. A. Sarver, THIS JOURNAL, 49, 1472 (1927).

[5] F. J. Watson, *Chem. Eng. Min. Review*, 20, 355, 396 (1928).

The oxidation was first studied qualitatively, various amounts of acid, indicator and dichromate being mixed at different temperatures, and the time noted at which the color first became perceptible. The results were not very exact since it was hard to perceive the first tinge of violet, due to a green which often accompanied it. The hue is somewhat dependent upon the acidity, being violet at low hydrogen-ion concentrations, and more blue in acid concentrations higher than 4 N.

The speed of oxidation is approximately proportional to the amount of dichromate added for a given amount of indicator, and to the amount of indicator used for a given amount of dichromate. Furthermore, the reaction velocity increases rapidly with the temperature, being about four times as great at 55 as at 25°.

Acids increase the speed of reaction very markedly, and the color develops much more quickly in hydrochloric than in sulfuric acid of the same normality, on account of the greater activity of the hydrogen ions in the former. This increased speed of oxidation in larger hydrogen-ion concentrations is explained by the fact that the oxidation potential of the dichromate increases rapidly with the acidity, whereas as we shall see later the potential of the system diphenylbenzidine and its violet oxidation product is practically independent of the concentration of the hydrogen ions. This explanation is supported by the behavior of diphenylamine and diphenylbenzidine with stronger oxidizing agents; e. g., with potassium permanganate the violet appears instantly at all acidities.

Mercuric chloride has a pronounced inhibiting effect, whereas traces of ferrous iron show an enormous accelerating effect; when both are present at the same time the iron only partially neutralizes the adverse action of the mercuric chloride. It may be mentioned that ferric iron is without any effect. Hence the oxidation is induced by the reaction between ferrous iron and potassium dichromate, which is in harmony with the primary oxide theory of Manchot. First, the ferrous ion is oxidized to an intermediate unstable higher oxidation state than ferric iron, which in turn reacts rapidly with diphenylbenzidine.

Finally it should be mentioned that in all cases where a large excess of oxidant was added, the violet color was quickly destroyed, becoming first red, then yellow, with dark flocks precipitating out after standing for some time, leaving a colorless solution in which it was impossible to get the violet again. The diphenylbenzidine violet is therefore decomposed in an irreversible way by excess oxidant.

II. Light Absorption by Diphenylbenzidine Violet.—The light absorption of the violet oxidation product of diphenylamine and diphenylbenzidine (which will be called diphenylbenzidine violet and abbreviated D.B.V.) in hydrochloric and sulfuric acids of various concentrations was determined by means of a Keuffel and Esser spectrophotometer and, in agreement with the experiments of Thiel,[6] the curves were found to be nearly flat between 5400 and 5700 Å., the absorptions differing by less than 1% over this range. The intensities of the colors increased more or less slowly with the time, according to the concentration of the acid, and later decreased, so that it was difficult to obtain comparable readings for the whole absorption curve at one time: at one stage they were practically constant for a few minutes, however, and by working rapidly fairly comparable values were obtained; but it was not possible to derive transmission coefficients under these conditions. A definite shift of the absorption maximum toward the longer wave lengths was observed in the stronger acid solutions, from 5600 Å. for the colored oxidation product from either indicator in 0.5 N hydrochloric or sulfuric acid to 5850 Å. for 6 N acid solutions. This agrees well with Thiel's value of 5870 Å. for diphenylamine in 50% sulfuric acid, considering that he worked at a still higher acidity. The fact that the colored oxidation products of both diphenylamine and diphenylbenzidine have identical absorption spectra is one proof that the two bases give identical compounds (see discussion, Section V).

III. Solubility of Diphenylbenzidine and the Order of its Ionization Constant.—The solubilities of diphenylbenzidine in water, in various concentrations of hydrochloric acid, sulfuric acid and sodium chloride, and in saturated mercuric chloride have been determined by a nephelometric method. A freshly prepared solution containing 0.04 mg. of diphenylbenzidine per cc. in a mixture of concentrated sulfuric and glacial acetic acids (10 and 90% by volume, respectively) was dispensed from a microburet, 0.01 cc. at a time, into 50 cc. of water or solution contained in a small beaker.[7] After each addition the solution was stirred, poured carefully (to avoid formation of air bubbles) into Nessler tubes, and compared with other tubes containing only the solvent, in a dark room in a simple nephelometer constructed from a photographic dark-room lamp. Solubilities were estimated from the minimum volume of standard solution required to give the faintest perceptible permanent cloud, and could be reproduced with an accuracy of about 10%, which is quite satisfactory for such extremely small values; the concentrations were so low that the solutions did not show any perceptible color with oxidizing agents. Solubilities estimated in this way for water both at room temperature and at 50° were 0.06 mg. per liter, while those for 0.5 N and N sodium chloride, and saturated mercuric chloride were 0.05 mg. per liter. Solubilities of diphenylbenzidine in various concentrations of hydrochloric acid and the corresponding hydrolysis constants of the base are given in Table I.

Although diphenylbenzidine is a diacid base, its first ionization constant

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[6] A. Thiel, *Z. Elektrochem.*, 35, 274 (1929).

[7] Soon after the preparation of diphenylbenzidine standard solutions, a green compound separated out; hence it was necessary to use fresh solutions.

TABLE I

SOLUBILITIES IN HYDROCHLORIC ACID AND HYDROLYSIS CONSTANT OF *DIPHENYLBENZIDINE* AT 25°

Normality of HCl	Mg. D.B. per liter	Mg. D.B.H$^+$ per liter	$K_{\text{Hydrolysis}}$	$K_{\text{Hydrolysis}}$ (corr. for salting out)
0.1	0.07	...	...	...
.25	.09	0.03	0.50	0.50
.5	.12	.06	.50	.45
1.0	.17	.11	.55	.50
2.0	.28	.22	.55	.51

is so small that the solubility in acids will be mainly determined by the magnitude of this constant, according to the equations:

$$\textit{Diphenylbenzidine} + \mathrm{H}^+ \rightleftharpoons \textit{Diphenylbenzidine}\,\mathrm{H}^+ \tag{1}$$

and

$$\frac{[a\mathrm{D.B.}][a\mathrm{H}^+]}{[a\mathrm{D.B.H}^+]} = \frac{[a\mathrm{D.B.}][\mathrm{H}^+]f\mathrm{H}^+}{[\mathrm{D.B.H}^+]f\mathrm{D.B.H}^+} = K_{\mathrm{Hydrolysis}} \tag{2}$$

where $[a\mathrm{D.B.}]$ is the activity of diphenylbenzidine and equals the solubility in water, $[a\mathrm{H}^+]$ is the activity of the hydrogen ion and $[a\mathrm{D.B.H}^+]$ that of the diphenylbenzidine cation. Since $f\mathrm{H}^+$ and $f\mathrm{D.B.H}^+$ represent the activity coefficients of univalent ions at the same ionic strength, their magnitude will be of the same order, and the ratio of activities can be assumed to be equal to the ratio of ionic concentrations; this may introduce an uncertainty of 5–10% at higher acidities, but it is not serious when the approximate nature of the solubility determinations is considered. The concentration $[\mathrm{D.B.H}^+]$ is equal to the difference between the solubilities of diphenylbenzidine in acid and in water, but should be corrected for the salting out effect of the electrolyte. In order to approximate the magnitude of this correction, the solubility of diphenylbenzidine was determined in N and 0.5 N sodium chloride solution, and the salting out effect was assumed to be the same in hydrochloric acid of corresponding concentrations. The activity of the diphenylbenzidine is not changed by the salting out, although the actual concentration may be reduced; hence it may be assumed to be equal to the solubility in water. So it follows that

$$\frac{[S_{\mathrm{W}}]\cdot[\mathrm{H}^+]}{[S_{\mathrm{A}} - S_{\mathrm{W}}]} = K_{\mathrm{Hydrolysis}}\ \textit{(uncorrected)} \tag{3}$$

and

$$\frac{[S_{\mathrm{W}}]\cdot[\mathrm{H}^+]}{[S_{\mathrm{A}} - S_{\mathrm{S}}]} = K_{\mathrm{Hydrolysis}}\ \text{(corrected)} \tag{4}$$

where S_{W} represents the solubility of diphenylbenzidine in water, S_{A} the solubility in acid and S_{S} that in salt solution, while the hydrogen-ion concentration is assumed to be equal to the normality of the acid.

In this way the hydrolysis constant (corrected for salting out effect) has been determined and found to be remarkably constant in acid concentrations between 0.1 and 2.0 N, with an average magnitude of 0.50 at 25°.

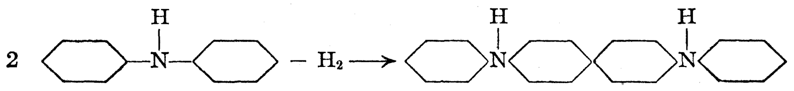
Hence the constant of the first ionization of diphenylbenzidine is 2×10^{-14} at 25°, whereas Thiel[6] found a value of 7.6×10^{-14} for diphenylamine at 15°.

The solubility of diphenylbenzidine in sulfuric acid is much smaller than in hydrochloric acid of corresponding normality, on account of the lower activity of the hydrogen ions in the former acid. In 4 *N* hydrochloric acid and 6 *N* sulfuric acid the solubility of diphenylbenzidine is much greater than could be expected from its behavior as a monoacid base; the activity of the hydrogen ions in these strongly acid solutions is much larger than the corresponding concentrations, and also the second basic group may play an important part in strong acid medium.

Finally, it is of interest to point out that since the solubility of diphenylbenzidine in saturated mercuric chloride is approximately the same as in water, we cannot explain the great inhibiting effect of this salt on the color development by the formation of a complex between it and diphenylbenzidine; so it seems more reasonable to suppose that it reacts in some way with the colored compound or intermediate products.

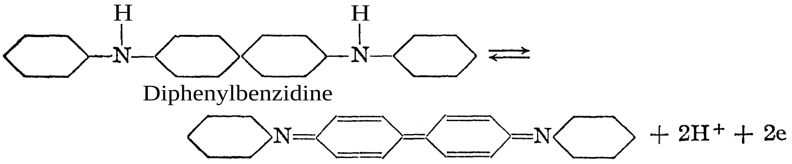
IV. Potentiometric **Titrations.**—Freshly prepared solutions of diphenylamine and diphenylbenzidine in various concentrations of sulfuric acid were titrated potentiometrically with 0.01 *N* potassium dichromate solutions containing the same concentrations of sulfuric acid as the titration mixtures, both at room temperature (24–30°) and at 50°. The bright platinum gauze electrode was ignited before each titration, and used in conjunction with a saturated calomel electrode with salt bridge of agar and saturated potassium chloride.

The experiments were not very satisfactory from the stoichiometric point of view, because of the slowness with which equilibrium is established and the occurrence of side reactions. However, it was found that the main reactions could be represented thus



Diphenylamine Diphenylbenzidine

(5)



Diphenylbenzidine

Diphenylbenzidine violet

(6)

The oxidation of diphenylamine to diphenylbenzidine is irreversible, and it even seems doubtful whether the reversible system, diphenylbenzidine $\rightleftarrows$ diphenylbenzidine violet, ever reaches a constant potential. In the first place they react with each other to form an extremely slightly soluble green meriquinoid (a molecular compound of diphenylbenzidine and diphenylbenzidine violet). Moreover, the diphenylbenzidine violet itself easily undergoes further oxidation by an irreversible reaction. Therefore the potentials observed in direct titrations depend upon the time which has elapsed since the addition of the oxidant, the temperature, the acidity and the amount of excess oxidant. Yet it is possible to obtain reproducible results when the titrations are made under similar conditions. When the dichromate is added rapidly the violet appears before complete oxidation of diphenylamine to diphenylbenzidine, but the color fades on standing and the potential drops. After the quantitative formation of the diphenylbenzidine, a continued addition of dichromate oxidizes it to diphenylbenzidine violet, but part of this reacts with unchanged diphenylbenzidine to form the green meriquinoid. This meriquinoid formation is less at higher temperatures than at room temperature.

The potentials observed during the oxidation of diphenylamine to diphenylbenzidine have no exact significance, because the reaction is irreversible and the electrode behaves more or less like an oxygen electrode, with the values decreasing on long standing. At the beginning of the oxidation of diphenylbenzidine to diphenylbenzidine violet the potentials are reproducible, although the meriquinoid formation and the decomposition of the violet are responsible for the fact that the potentials are never constant for an indefinite time.

In Table II a summary is given of the results found in a few examples taken from a large number of direct titrations of 1.69 mg. of diphenylamine with 0.01 *N* potassium dichromate at different acidities and temperatures.'. The table is self-explanatory with the exception of the last two columns; of these, the former gives the number of equivalents of oxidant added before a violet color was perceptible in the solution (which point could be only approximated, since the green greatly obscured the violet), and the latter column indicates the potential (against saturated calomel electrode) at which the violet was first visible in the solution. Probably there was already some violet in the solution before it could be perceived, on account of being masked by the green; this could be inferred from the results of the back titrations, as will be shown later. The violet was generally first observed at potentials of 0.510–0.525 v. (against saturated calomel electrode) when the titrations were made in the presence of ferrous iron.

These results show that in the direct titration of diphenylamine two jumps in potential are observed under the proper conditions, the first corresponding to the complete oxidation of diphenylamine to diphenylbenzidine, the second to the complete oxidation of the latter to diphenylbenzidine violet. The last does not correspond exactly to the stoichiometric value on account of the fact that the green insoluble meriquinoid formed during the titration is attacked very slowly (tending to cause low

TABLE II

DIRECT TITRATIONS OF DIPHENYLAMINE WITH POTASSIUM DICHROMATE

50-cc. portions of acid of the designated normality containing 1.69 mg. of diphenytamine used for each titration

		First *jump* (D.A. → D.B.)		Second *jump* (D.B. → D.B.V.)		Violet first perceptible	
H_2SO_4, N	*Temp.*, °C.	Equiv. of oxidant required (calcd. 1.0)	Approx. e. m. f. (against satd. C.E.), v.	Equiv. of oxidant required (calcd. 2.0)	Approx. e. *m*. f. (against satd. C.E.), v.	*Equiv.* of oxidant required (calcd. 1.0)	Approx. *e. m.* f. (against satd. C E), v
0.1	27	1.0	0.550	2.0	0.580	1.1	0.555
.1	25	0.95	.530	2.2	.580	1.2	.560
.1	50	.9	.525	1.9	.570	0.9	.590
.1	50	.9	.535	1.9	.580	.95	.530
.25	25	1.0	.545	2.2	.590	1.1	.558
.25	50	1.0	.550	2.2	.600	1.1	.550
.25	50	1.0	.550	2.2	.600	1.1	.555
.5	25	1.1	.535	2.2	.600	1.0	.530
.5	25	1.1	.540	2.3	.605	1.1	.538
.5	50	0.95	.530	2.1	.600	0.6	.510
.5	50	1.0	.530	2.1	.605	.4	.505
.5	50	1.0	.525	2.1	.605	.8	.518
1.0	28	1.0	.530	2.0	.600	.9	.524
1.0	50	1.1	.520	2.0	.590	.7	.530
1.0	50	1.1	.530	2.0	.595	.8	.520
1.0	50	1.1	.530	2.2	.600	.9	.530

results), and because part of the diphenylbenzidine violet is oxidized irreversibly to other products (tending to cause high results).

Similar titrations have been made with diphenylbenzidine under the same conditions of time and acidity, which confirm the results obtained with diphenylamine; but, owing to the slight solubility of the former, still more difficulties were encountered. Of course, only one jump in potential occurs in this titration, after the complete oxidation to diphenylbenzidine violet.

On account of the fact that equilibrium is established fairly slowly in direct titrations, with much opportunity for side reactions, it was thought desirable to add the diphenylamine or diphenylbenzidine to a small excess of dichromate and then back-titrate as quickly as possible. It is inevitable that some of the diphenylbenzidine violet will be further oxidized by the excess dichromate when working in this way; but by making the excess small and working rapidly it has been possible to obtain reproducible results which confirm the proposed theory of the reaction mechanism. The oxidized solutions were kept at room temperature until the excess dichromate had been reduced with ferrous iron, in order to minimize further oxidation of the diphenylbenzidine violet; they were then warmed to 50° for the rest of the titration, to hasten the establishment of equilibrium. Two jumps in potential were observed, the first corresponding to the complete reduction of the excess dichromate, and the second to the completion of the reduction of the diphenylbenzidine violet to the meriquinoid, diphenylbenzidine green. Averaging the results of a large number of titrations of diphenylamine at different acidities, it was estimated that after the removal of excess dichromate, 2.01 equivalents of the oxidant had been consumed by the diphenylamine (calcd., 2.0), and that the potential at the equivalence point was 0.575 v. (against saturated calomel electrode); likewise, the second jump, corresponding to the complete reduction of the diphenylbenzidine violet to diphenylbenzidine green, indicated that 1.62 equivalents of oxidant were required to oxidize the original diphenylamine to diphenylbenzidine green (calcd., 1.5), and the potential at this equivalence point was 0.510 v. (against saturated calomel electrode). Such a back-titration is shown graphically in Fig. 1, where the first part of the curve represents the reduction of the excess dichromate by ferrous sulfate, and the portion following the first break shows the reduction of diphenylbenzidine violet to the meriquinoid, diphenylbenzidine green, the second break indicating this equivalence point.

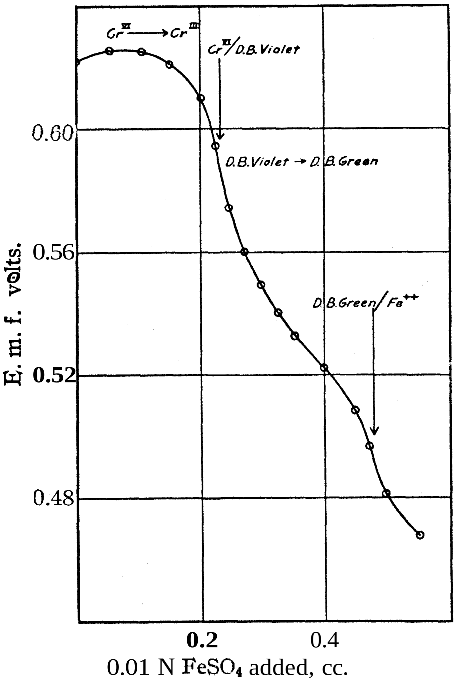


Fig. 1.—Back titration of diphenylbenzidine violet and excess potassium dichromate in 0.6 N sulfuric acid.

Similar experiments were made with diphenylbenzidine, but were less satisfactory from the stoichiometric point of view, for the reasons previously given; in all cases, however, the color change from violet to green took place at the same potential as with diphenylamine, 0.51 ± 0.01 v. (against saturated calomel electrode), or 0.76 ± 0.01 v. (against normal hydrogen electrode). It is striking that the potential at which this color change takes place is very constant, and quite independent of the acidity. Hence, it may be concluded that diphenylamine and diphenylbenzidine give their violet oxidation product in solutions having higher oxidation–reduction potentials than those mentioned above, at all reasonable acid concentrations. In general, the curves representing the potentials during the reduction of diphenylbenzidine violet to diphenylbenzidine green have the same shape, and corresponding points have the same potentials at all acidities between 0.1 and 1.0 N.

Further, although the results have no exact quantitative significance, they confirm the reaction mechanism represented by Equations 5 and 6.

V. Discussion.—1. The potentiometric experiments show that upon slow addition of a strong oxidizing agent to a solution of diphenylamine in an acid medium, one equivalent of oxidant is consumed before the violet is formed. Moreover, before the solution becomes colored, a milky cloudiness is observed, probably from diphenylbenzidine, which is very slightly soluble. That diphenylbenzidine is indeed the first oxidation product obtained from diphenylamine was proved by the following experiment. To a liter of a solution of 100 mg. of diphenylamine in 0.1 N sulfuric acid, 90% of the theoretical amount of dichromate necessary for the oxidation to diphenylbenzidine was added slowly at 50°. The solution soon became opalescent, with a tinge of green from the chromic salt formed. The white insoluble substance coagulated immediately upon boiling, and was filtered off and washed first with water and then alcohol. The residue was recrystallized from boiling toluene and dried at 105°. The melting point of this product was 244–245° (uncorr.), and the same value (within 2°) was found for a mixture of this with pure diphenylbenzidine.[8]

This experiment partly confirms the important work of Kehrmann and Micewicz,[9] who were the first to clear up the reaction mechanism in the oxidation of diphenylamine. Although the colored oxidation products of diphenylamine had been known and studied for a long time, the interpretations of the reaction given by various writers[10] were quite contradictory. Kehrmann and Micewicz obtained tetraphenylhydrazine, then diphenylbenzidine, then a green oxidation product of diphenylbenzidine which they called a half-quinoid salt, or quinhydrone, and, finally, the blue holoquinoid salt. Further strong oxidation gave a yellow solution, and then, by molecular rearrangement, a red solution. Dilute acid solutions of all these quickly became colorless, with precipitation of greenish-black flocks. These results were confirmed in the main by a number of writers, especially Marqueyrol and Muraour,[11] except that the latter obtained only traces of

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[8] It should be mentioned that there is some confusion in the literature as to the correct melting point of diphenylbenzidine. R. Gnehm and H. Werdenburg [*Z. angew. Chem.*, 43, 1027, 1051, 1128 (1899)] gave it as 246–248°; V. Kadiera [*Ber.*, 38, 3575 (1905)] reported it as 242°, corrected; and M. Marqueyrol and H. Muraour [*Bull. soc. chim.*, 15, 186 (1914)] found 250.5–251.5°.

[9] F. Kehrmann and St. Micewicz, *Ber.*, 45, 2641 (1912).

[10] A. W. Hoffmann, *Ann.*, 132, 160 (1864); V. Merz and W. Weith, *Ber.*, 5, 283 (1872), communicated by O. Meister; R. Gnehm and H. Werdenburg, *Z. angew. Chem.*, 43, 1027, 1051, 1128 (1899); A. Baeyer, *Ber.*, 38, 583 (1905); V. Kadiera, *ibid.*, 38, 3575 (1905); F. D. Chattaway and H. Ingle, *J. Chem. Soc.*, 67, 1090 (1895); H. Wieland and S. Gambarjan, *Ber.*, 39, 1499 (1906).

[11] M. Marqueyrol and H. Muraour, *Bull. soc. chim.*, 15, 186 (1914); *Ann. chim. anal. appl.*, 19, 174 (1914); H. Wieland, *Ber.*, 46, 3296 (1914); *ibid.*, 52, 886 (1919); H. Wieland and C. Müller, *ibid.*, 46, 3304 (1914).

diphenylbenzidine when tetraphenylhydrazine was taken as the starting substance. At first Wieland believed that each molecule of diphenylamine splits off one molecule of hydrogen (as H_2O) upon osidation, to give the bivalent radical $[Ph—N{=}C_6H_4]{=}$, which then polymerizes to the blue product $Ph—N{=}C_6H_4{=}C_6H_4{=}N—Ph$; but Marqueyrol and Muraour showed by quantitative experiments that diphenylbenzidine is indeed the main product, and Wieland later concurred in their conclusions.

An interpretation similar to the original one of Wieland has recently been offered by Thiel,[6] but he assumes that not the free amines, but the corresponding cations, enter into reaction. Although it is quite possible that the formation of the bivalent cation depends upon working conditions (acidity, temperature, solvent, etc.), the present paper shows definitely that at fairly low acidities (0.1–2.0 N) with slow addition of the oxidizing agent, diphenylbenzidine is the first product which can be isolated.

Hence, it is felt that the first stage in the oxidation of diphenylamine is correctly represented by Equation 5 (Section IV), since the formation of diphenylbenzidine in nearly stoichiometric amounts has been proved, while no evidence of the formation of intermediate compounds has been found.

2. Diphenylbenzidine may be further oxidized to the violet or blue holoquinoid salt, diphenylbenzidine violet, by a reversible reaction Equation 6, (Section IV). This diphenylbenzidine violet is a very unstable compound, and is easily oxidized further to yellow or red compounds whose composition is as yet unknown; or it may react with unchanged diphenylbenzidine to form the greenish-black meriquinoid, diphenylbenzidine green. In fact, it is possible to titrate the color out of an oxidized diphenylbenzidine solution by adding a solution of pure diphenylbenzidine. While it is impossible to state with certainty, it is believed that diphenylbenzidine green is an equimolecular compound of oxidized and unoxidized diphenylbenzidine.

3. This meriquinoid, diphenylbenzidine green, which was first mentioned by Kehrmann and Micewicz,[9] is an extremely slightly soluble green substance, and obscures the perception of the violet in the solution. A saturated solution of it in water or acid is colorless, and contains so little diphenylbenzidine that it is not colored by an oxidizing agent. A suspension of the green product is, however, changed to violet by dichromate or any strong oxidizing agent, which shows the presence of diphenylbenzidine in the compound. On account of its extremely slight solubility, it is hard to reduce it with ferrous sulfate, but stronger reducing agents like stannous chloride discharge the color rapidly, and a milky white opalescence from the diphenylbenzidine remains. If diphenylbenzidine violet is titrated potentiometrically with ferrous sulfate, a jump in potential occurs at the point where all the violet has been reduced to the green meriquinoid; if, however, the ferrous sulfate is added very rapidly, the formation of the

green product is prevented, and the reduction goes as far as diphenylbenzidine. The stability of a suspension of the meriquinoid decreases with the temperature; at 50° it shows a weak violet color, which indicates that the dissociation of the molecular compound is greater at 50° than at room temperature.

4. If a small excess of potassium dichromate is added either to diphenylamine or diphenylbenzidine, both indicators behave identically upon back-titration with ferrous sulfate, which shows that the oxidation product is the same in both cases; this conclusion is also confirmed by the similarity of the absorption spectra (Section II).

5. It seems very remarkable that the potential at which the violet changes to green is independent of the acidity, at about 0.51 ± 0.01 v. against saturated calomel electrode, or at about 0.76 ± 0.01 v. against the normal hydrogen electrode, even the temperature having a negligible effect on this value. It was shown by special experiments that even at PH values of 3 to 4, the change from violet to green takes place at approximately the same potential, although the diphenylbenzidine violet itself is extremely unstable at these low acidities.

According to Equation 6 (Section IV) the oxidation–reduction potential should be

$$E = E_0 + \frac{0.060}{2} \log \frac{[a\text{D.B.V.}][a\text{H}^+]^2}{[a\text{D.B.}]}, \text{ at } 30^\circ \qquad (7)$$

where a designates the activity of the specified substance or ion. Therefore one would expect that E would increase 60 millivolts for each decrease of 1 in the PH.

Now if we consider the system diphenylbenzidine violet $\rightleftarrows$ diphenylbenzidine green, especially at the moment when the violet changes to green, we can safely assume that [aD.B.] is a constant, because diphenylbenzidine is very slightly soluble and its activity in a saturated solution will be a constant (cf. Section III). The diphenylbenzidine violet, on the other hand, had a variable concentration; further, part of it is present as cation (also violet or blue), and part as the free base, the latter determining the potential, according to the equations

$$\text{D.B.V.} + 2\text{H}^+ \rightleftarrows \text{D.B.V.H}_2^{++} \qquad (8)$$

$$[a\text{D.B.V.}] = \frac{[a\text{D.B.V.H}_2^{++}]}{[a\text{H}^+]^2} \cdot K \qquad (9)$$

Now, if diphenylbenzidine violet is a relatively strong base, as compared with diphenylbenzidine itself (which seems probable), practically all the dyestuff will be present as cation in the fairly strong acid solution. Therefore, if we consider the [D.B.V.] at different PH values, but at the same total concentration of dyestuff (free base + ions), then we may assume that [D.B.V.H_2^{++}] is practically the same in all the solutions, while the concentrations of the free base are quite different.

Assuming [aD.B.] a constant, we have from Equation 7

$$E = E_0' + \frac{0.060}{2} \log\, [a\text{D.B.V.}][a\text{H}^+]^2 \tag{10}$$

or, since

$$[\text{D.B.V.}] = \frac{[\text{Total dyestuff}]}{[a\text{H}^+]^2} K \text{ approximately} \tag{11}$$

we derive by substitution

$$E = E_0'' + \frac{0.060}{2} \log \frac{[\text{Total dyestuff}][a\text{H}^+]^2}{[a\text{H}^+]^2} = E_0' + 0.03 \log\, [\text{Total dyestuff}] \text{ approximately} \tag{12}$$

It thus becomes comprehensible why the oxidation–reduction potential is independent of the acidity, although it must be emphasized that the above relations hold only approximately.

6. It has already been mentioned that diphenylbenzidine violet can be oxidized to other products; at low acidities, especially, it is very unstable. In solutions with a P_H of 7 to 2, potassium dichromate is not able to oxidize diphenylamine or diphenylbenzidine to the violet; but potassium permanganate, on the other hand, oxidizes both indicators easily at these acidities, due to its higher oxidation–reduction potential. The violet is the more easily destroyed, the lower the P_H and the higher the oxidation–reduction potential; in acetic acid medium, the violet produced by oxidizing diphenylamine with permanganate disappears almost instantly.

7. Potentiometric titrations have been made in the presence of mercuric chloride in order to see whether this substance has a specific effect upon oxidation–reduction potentials, but it was not possible to make satisfactory measurements. Even the ferrous iron–dichromate titration was impossible; the electrode was slow, and no jump in potential occurred at the equivalence point. It seems that the electrode takes up some mercury by polarization, and does not respond quickly to excess of oxidant. This may be of significance in the use of a bimetallic electrode system.

Summary

1. At acidities between 0.1 and 2.0 N, diphenylamine is oxidized quantitatively to diphenylbenzidine by potassium dichromate if the oxidant is added slowly to the former solution. Further addition of dichromate oxidizes the diphenylbenzidine to a violet quinoid salt, which quickly combines with unchanged diphenylbenzidine to form an extremely slightly soluble green meriquinoid salt.

2. In titrating diphenylbenzidine violet with ferrous sulfate the color change, violet to green, takes place at a potential of about 0.51 v., against saturated calomel electrode; or at 0.76 v., against the normal hydrogen electrode, regardless of the hydrogen-ion concentration of the solution. An explanation has been offered to account for this.

3. The results of the analytical study are not very satisfactory from the stoichiometric point of view, because side reactions may occur, diphenylbenzidine and diphenylbenzidine green are very slightly soluble, and diphenylbenzidine violet decomposes rapidly, especially at low acidities.

4. The absorption spectra of oxidized diphenylamine and diphenylbenzidine solutions have been determined and found to be identical; the maxima of the curves are very flat, and shift toward the longer wave lengths in stronger acid solutions.

5 The solubility of diphenylbenzidine in water is 0.06 ± 0.005 mg. per liter at 25–50°; and its ionization constant at 25° is of the order of 2×10^{-14}.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

STUDIES IN INTENSIVE DRYING[1]

BY E. JUANITA GREER[2]

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The following is an account of an experimental study of the intensive drying, and therewith "the catalytic" effect of small traces of water, mainly in liquid benzene, which leads to an explanation of the phenomenon observed. Since Baker's work was published in 1922 there has been a constant stream of theoretical explanations of intensive drying, as well as a large number of experimental studies dealing with this strange phenomenon.

It is unnecessary in this paper to give even a synopsis of either the theoretical or the experimental aspects of this problem, inasmuch as quite recently this whole subject has been carefully and most adequately reviewed in book form under the title of "The Effects of Moisture on Chemical and Physical Changes," by J. W. Smith.[3]

Suffice it to say that since Baker's[4] paper data have accumulated which tend to support, and lately some as justly to contest, the view that when the last traces of water are removed from certain liquids, there occur physical changes in the latter that are consistent with the assumption of an association of the molecules in the liquid. The properties investigated have been such as the boiling point, freezing point, density, vapor density, surface tension, latent heat of vaporization and vapor pressure. However,

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[1] Based on a dissertation submitted June, 1929, to the Board of University Studies of the Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Holder of the Boston Alumnae Fellowship of the American Association of University Women for 1929–1930, when this work was completed.

[3] Longmans, Green and Co., 1929.

[4] Baker. J. *Chem. Soc.*, 121, 568 (1922).

from a theoretical and practical consideration of the work of other investigators, it was assumed when this work was begun in 1927 that the vapor pressure of the liquids was the property the least open to misinterpretation and also the most reliable from the standpoint of experimental technique. This work began with the purpose of finding a means of producing liquids exhibiting the intensive drying effect in a shorter time than previously in order that the phenomenon might be more readily investigated.

Experimental Part

The Possibility of Compound Formation with Phosphorus Pentoxide and Benzene.—In the course of the preliminary work, benzene that had been purified by the method used by Hill[5] was found to produce color in pure phosphorus pentoxide when the mixture was stored in the light. The phosphorus pentoxide was prepared by resubliming Baker's pure phosphoric anhydride in a current of pure oxygen according to the method of Finch and Fraser[6] and the product satisfied the requirements of Baker[7] and of Finch and Peto[8] for purity.

Experimental investigation indicated that small traces of impurities in benzene—mainly sulfur compounds such as thiophene and carbon disulfide—are capable of imparting color to phosphorus pentoxide, varying from pale grayish-pink to yellow, when a mixture is stored in the light.

An investigation of the methods more generally used for the purification of benzene rarely revealed attempts to eliminate carbon disulfide which along with thiophene is one of the chief contaminants of commercial benzene.

Rigid purification of benzene either by an extension and combination (1) of the methods of Goldberg[9] and Haller and Michel[10] or (2) of the methods of Goldberg and Victor Meyer[11] which proved to be the more convenient method—gave a product which distilled within 0.01° and failed to impart any color to the phosphorus pentoxide upon heating or after a year's exposure to light.

The increased boiling points reported by Baker were ascribed by Balarew[12] possibly to the formation of compounds with phosphorus pentoxide and benzene. A search of the literature revealed that Giran[13] reported definite, solid, colored compounds insoluble in benzene resulting from the reaction of phosphorus pentoxide and benzene. As stated previously, impure

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[5] Hill, THIS JOURNAL, 44, 1168 (1922).

[6] Finch and Fraser, J. *Chem. Soc.,* 117 (1926).

[7] Baker, *ibid.,* 121, 569 (1922).

[8] Finch and Peto, *ibid.,* 121, 693 (1922).

[9] Goldberg, *Z. angew. Chem.,* 4, 75 (1899).

[10] Haller and Michel, Bull. *soc. chim.,* [3] 15, 1065 (1896).

[11] Victor Meyer, *Ber.,* 18, 1489 (1885).

[12] Balarew, *J. prakt. Chem.,* 116, 57 (1927).

[13] Giran, *Compt. rend.,* 126, 592 (1898); *ibid.,* 129, 965 (1899).

benzene did impart similar colorations to pure phosphorus pentoxide, but this present investigation indicated no such compounds as described by Giran with pure benzene and pure phosphorus pentoxide. Moreover, a fused glass apparatus containing a differential mercury manometer such as is described in the following section of this paper revealed no decrease in the vapor pressure of impure benzene dried with phosphorus pentoxide for two years. This would indicate that even if a compound were formed in the impure benzene, it was insoluble as Giran reported, and had no measurable vapor pressure, thus causing no change in the vapor pressure of the benzene.

Experiments with Phosphorus Pentoxide and Fused Glass Apparatus.—In 1926, Smits[14] reported that capillary-free glass hastened the drying of liquids with phosphorus pentoxide. His glass surfaces were fused and then cleaned with chromic acid, washed, steamed and dried. This chromic acid treatment has been shown by other investigators[15] to etch the surface of the glass. In order to preserve the beneficent effects of a fused pyrex glass surface, the apparatus used in the present investigation was first cleaned with chromic acid and, in the usual manner, washed with water and dried. It was then fused by an expert glass blower who melted the glass completely and then shaped it, blowing at all times through a tube of phosphorus pentoxide to avoid the access of water to the apparatus.

The entire apparatus of the circulating and of the static types similar to those used by Smits,[14] was constructed of fused glass and contained a differential mercury manometer to indicate the difference in pressure between the benzene being dried with phosphorus pentoxide on the one side, and a sample of the same normal benzene in a fused glass bulb on the other side. The vessels were filled under moisture-free conditions by the passage of a stream of air dried with phosphorus pentoxide. The liquids were frozen with solid carbon dioxide and ether when the apparatus, evacuated thoroughly by using a mercury diffusion pump in series with a high vacuum oil pump, was sealed off. The manometer was then filled with dry mercury from a reservoir in the apparatus by tilting the latter slightly.

No difference between the vapor pressures on the two sides of the pieces of apparatus has been observed even after three years in one case and twenty-seven months in two other cases. Moreover, in defense of Baker when his work was attacked by Balarew,[12] Smits[16] reported that he could detect no vapor pressure change in some of his pieces of apparatus after two years' drying.

Experiments with Silica Gel and Benzene.—A preliminary experiment

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[14] Smits, *J. Chem. Soc.*, **2655** *(1926).*

[15] **Frazer, Patrick** *and* Smith, *J. Phys. Chem., 31,* 897 *(1927)*

[16] Smits, *Z. physik. Chem.*, **129**, **33** *(1927)*

using pure, activated silica gel as the drying agent indicated a definite decrease in the vapor pressure of benzene. This drying effect appeared within twenty-four hours and seemed to have reached complete equilibrium after being kept for five days in a thermostat at 25°.

Apparatus of the type shown in Fig. 1 was constructed and joined in ring form. The differential manometer M contained pure mercury which was heated in the manometer with pumping for several hours to remove dissolved air and moisture. The pumps continued while the whole apparatus was heated well with a carbon flame to remove surface moisture and tested for leaks with a spark coil.

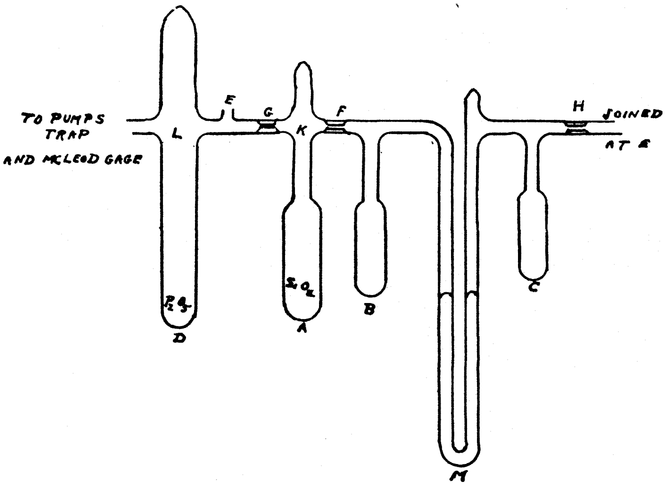

Fig. 1.

After the purified silica gel,[17] activated at 500°, was sealed up in vessel A, tube D was cracked and filled with pure phosphorus pentoxide and benzene, purified by the methods recommended earlier in this paper. Point L was plugged with glass wool to retain the phosphorus pentoxide used for the preliminary drying of the benzene. Tube D was quickly sealed while its contents were frozen with liquid air. The system was then evacuated to 10^{-5} mm. using an oil pump in series with a two-stage mercury diffusion pump. The liquid in D was melted, boiled, frozen with liquid air and opened to the pumps to remove dissolved air. This deaeration was repeated at least three times, or until no further air was removed by the process. The benzene was then distilled from D into vessels B and C simultaneously by immersing them in liquid air and removing the refrigerant from D. The apparatus was then pumped down to 10^{-5} mm. while the silica gel was heated to remove adsorbed liquid. The apparatus was sealed off at H while the pump continued and the silica gel in A was then

[17] Patrick, Frazer and Rush, *J. Phys. Chem.*, 31, 1511 (1927).

heated for half an hour with a large air flame which was kept in constant motion to prevent collapse of **A.** The apparatus was sealed off at G at a pressure of 10^{-5} mm. of mercury. The liquid air was removed from B and C when the silica gel had become cold and the benzene in B was allowed to distil onto the activated silica gel.

This method was used with pure benzene, pure carbon tetrachloride and pure carbon disulfide. With each a decrease in vapor pressure was observed upon drying the liquid with activated silica gel. Out of the nine pieces of apparatus that lasted through the above treatment without breaking, only one failed to manifest a decrease in pressure on the dry side.

Results.—These vapor pressure differences were measured at constant temperatures by means of a cathetometer and were checked to be certain that equilibrium had been attained. The vapor pressure differences observed for one liquid varied somewhat from one apparatus to another, as for example

Liquid	*T*, °C.	AP, mm.
CCl_4	0	3.67
CCl_4	0	3.30

Likewise, the vapor pressure differences varied among the different liquids as is shown by examples in Table I and plotted in Fig. 2. These values were taken at definite points as the temperature of the thermostat was raised from 20 to 50°, and were checked as it was lowered from 50 to 20°.

TABLE I

VAPOR PRESSURE DATA

Liquid (1) Benzene		Liquid (2) Carbon Tetrachloride		Liquid (3) Carbon Disulfide	
T, °C.	AP, mm.	T, °C.	AP, mm.	*T*, °C.	AP, mm.
−80.0	0.0	−80.0	0.0	−180.0	0.0
0.0	3.13	0.0	3.67	0.0	3.35
5.7	5.07	21.8	6.53	10.5	7.00
11.0	5.92	31.1	6.88	14.8	10.20
20.8	7.54	40.8	7.24	16.4	11.92
25.6	8.40	48.3	7.54	18.9	13.84
27.2	8.83			21.0	15.85
34.7	10.33			23.2	18.46
38.3	11.24				
45.5	12.71				
50.6	13.76				

These differences are all of similar order of magnitude and in the same direction as those reported in the De Liefde dissertation,[18] and there were no differences manifested at −180.0 and −80.0°, showing that the systems were air-free and that the differences were not due to dissolved air or gas.

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[18] W. C. De Liefde, "Dissertation," Amsterdam, 1927,

Experiments with Liquids Dried with Silica Gel.—In the course of the investigation of these liquids dried with silica gel, attempts were made to study the effect of the replacement of water, the "catalyst," which according to the theory of Smits[19] and Baker[20] is removed by prolonged or intensive drying and causes measurable changes in the molecular complexity of certain substances.

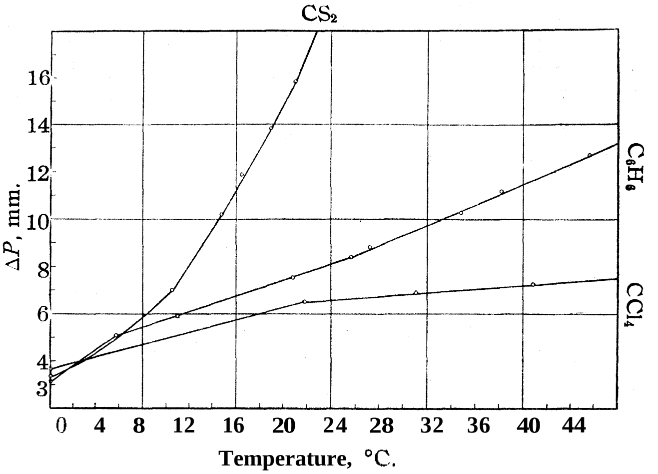

Fig. 2.

In order to effect the addition of moisture to benzene, the silica gel bulb was removed from the dry side of one piece of apparatus which was sealed to a series of bulbs and the pumping system. The mercury manometer had been frozen to act as a seal between the two sides of the apparatus. Silica gel at a saturated vapor tension of 4.5 mm. of water was added to the dry liquid, frozen with liquid air and the system was evacuated. The manometer which should have been level because of the replacement of the "catalyst" showed, however, a pressure difference of roughly 2.5 mm. at room temperature instead of the previous 7 mm. with the dry material alone. After distilling the benzene onto phosphorus pentoxide to remove the moisture and sealing off the silica gel that had been added, the benzene again manifested the previous 7 mm. pressure difference at 20°.

Discussion

The behavior studied in the above experiments in intensive drying indicated no catalytic action, but merely the addition of the partial pressure of water. It strengthened the theory that the difference in vapor pressure was due, not to the catalytic effect of the removal of water from the benzene

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[19] Smits, *Z. physik. Chem.*, 100, 477 (1922).

[20] Baker, *J. Chem. Soc.*, 949 (1927).

on the dry side, but to the presence of a minute trace of moisture in the benzene on the normal side.

Objections to the above view on the basis of Raoult's law are precluded because that relation demands a large mole fraction of water to produce a partial pressure equal to the pressure differences manifested in this set of investigations where the phenomenon was observed only in liquids in which water is very insoluble, as benzene, carbon tetrachloride and carbon disulfide.

In this work the amount of normal benzene used for comparison with the dried material was very small, varying from one to three grams in the different pieces of apparatus. The solubility of water in benzene at 20° is reported in the "International Critical Tables" as 0.057%. A rough calculation shows that the production at 20° of a partial pressure of 7 mm. of water vapor in one gram of benzene requires only 2.29×10^{-4} g. or 1.27×10^{-5} mole of water. This follows from the relation $P_p/P_s = X/X_s$ where $P_p = 7$ mm., $P_s = 17.363$ mm., the vapor pressure of water, necessary to saturate one gram of benzene at 20°; and $X_s = 0.00057$ g. of water.

However, according to Raoult's law, one gram of benzene requires 9.28×10^{-2} g. or 5.16×10^{-3} mole of water to produce a partial pressure of 7 mm. of water. This concentration of water is 405 times greater than that calculated from the solubility data above.

Moreover, upon analysis of Fig. 2, the curves for carbon disulfide, benzene and carbon tetrachloride seem very definitely to represent the vapor pressure of solutions of water in those liquids. The three curves show that the vapor pressure deviations from the normal are within a close range at 0°. From this point they converged and diverge again according to the extent of saturation and the change in solubility of water in the liquid with increasing temperature. The curve for benzene with its abrupt change in slope at the melting point of benzene is an excellent illustration of the increasing solubility of water in benzene with temperature.

An explanation of the mode of access of the minute quantities of water required to produce the effects may lie in any of several factors. However, it cannot have come from the benzene, which was dried with phosphorus pentoxide and distilled from it. The moisture may have come from the activated silica gel when it was heated before vessel C of Fig. 1 was sealed off, or from the glass during the sealing process.

In either case, the liquid air with which vessel C and its normal contents were frozen is a very powerful dehydrating agent and might easily have condensed a trace of moisture before it reached the pumps. Another source, despite the preheating described, is the deeper seated moisture in the walls of vessel C. This possibility is compatible with the conditions and observations of this investigation, since the vapor pressure difference was not always immediately apparent. It is supported by the investigation of Baker,[21] who by using sodium amalgam in a glass bottle dried at 150° found that bubbles of hydrogen began to appear after two days and concluded that "since these did not appear within twelve hours, their formation could not be ascribed to surface water," but to the deeper seated moisture.

The gradual emerging of the deeper seated moisture may possibly account for some of the vapor pressure differences observed in intensive drying experiments by other investigators. An experiment in which pure, dry air-free benzene was distilled from phosphorus pentoxide onto pure silica gel—originally saturated with water—which had been pumped down to 10^{-4} mm. pressure, showed that the benzene can displace some of the water adsorbed in the gel, for within six hours a steady pressure of 1 mm. was manifest in one case and 1.4 mm. in another case.

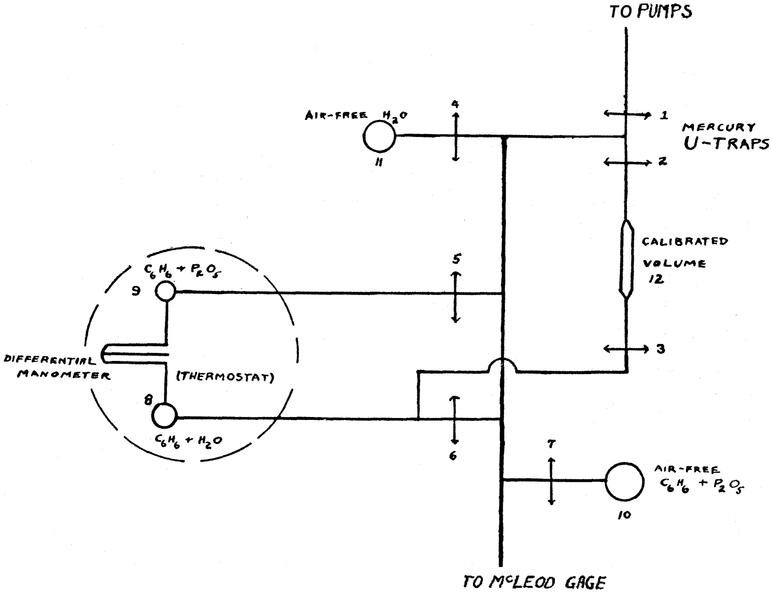

Fig. 3.

Experiments **with** Solutions of **Water** in Benzene.—As a confirmation of the calculations and experiments with silica gel and in an effort to test the theory that the vapor pressure changes observed were due to the presence of minute traces of moisture in the normal liquid instead of to intensive drying effects in the dried material, an apparatus was constructed to measure the change of vapor pressure of benzene with the addition of known amounts of water.

A diagram of the apparatus is shown in Fig. 3. The previous experiments had indicated the need of an absolute as well as a differential manometer which resulted in a three branched instrument, as shown, carefully

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[21] Baker, *J. Chem. Soc.*, 1663 (1929).

filled in *vacuo* with pure, redistilled, dry, air-free mercury. The air-free water and the air-free dry benzene were prepared by intermittent boiling and pumping the liquids until the residual air pressure could not be measured with the pressure gage. The mercury U-traps (1) through (7) were filled with pure mercury which was boiled out in the trap to remove moisture and air.

The glass was cleaned with chromic acid and washed with distilled water before use and the apparatus was carefully heated all over before being used for the experiment.

The pumping system consisted of a high-vacuum oil pump in series with a two-stage mercury diffusion pump.

The thermostat was constructed elevator style so that the tank could be raised and lowered when large temperature changes were necessary. It was set at 20.89° and with continuous cooling, intermittent heating and rapid stirring was regulated to 0.005°—never more than 0.01°—by a mercoid relay and a metastatic regulator. The thermostat was always kept at least 2.5" cooler than the room in order to prevent condensation outside of the bath.

The volume of vessel (8) was etched in increments of about 1 cc. and was calibrated by weighing water; and calibrated volume (12) was determined directly as 65.578 cc. by use of a gas buret.

Rigidly purified benzene, dried with phosphorus pentoxide was used as the liquid to be studied.

Manipulation and Results.—After the system had been dried out and evacuated to 10^{-5} mm. of mercury, the benzene in storage vessel (10) was frozen with ice and benzene was distilled into vessel (9), containing phosphorus pentoxide, and vessel (8) which were immersed in ice and salt. The vessels were then closed off with mercury traps and the remainder of the system was evacuated to 10^{-5} mm. A preliminary determination of the vapor pressures of the benzene in (8) and (9) at 20.89° showed both to be equal to 7.88 cm., so there was no moisture present at the beginning. Vessel (8) contained 25.635 cc. of pure benzene at 20°.

Water was then added in small quantities, representing about one-tenth of the saturation value, to the benzene in (8) by closing trap (1) and opening the calibrated volume (12) to the air-free water stored in (11) at 25°. After closing the traps and measuring the pressure and temperature of the known volume of water vapor in (12), trap (3) was opened and the water vapor was condensed in (8) which was frozen with a mixture of carbon dioxide and ether. The room temperature during this operation was always 25° or above. Trap (3) was closed and the remainder of the system was evacuated after each addition of water vapor.

The total volume between (8) and traps (3) and (6) was determined from the relation $P_1/P_2 = V_2/V_1$ at 24.2' by condensing water vapor of known pressure and volume (12) into empty vessel (8) by the method described in the preceding paragraph. The volume of liquid benzene was subtracted from this value and the difference was 116.2 cc., the volume of vapor in equilibrium with the liquid. By use of the relation $PV = nRT$ the amount of water present in the vapor and that dissolved in the liquid benzene in the successive solutions was calculated. Equilibrium was attained very slowly.

Results

TABLE II

EXPERIMENTAL DATA

Volume of benzene, 25.635 cc.; volume of vapor, 116.2 cc.; average temperature of vapor, = 22°.

	Total mole H_2O added	Partial press. of Hz0 in mm. at 20.89°	Mole H_2O in vapor	Mole H_2O in benzene
1	8.77×10^{-5}	1.87	1.17×10^{-5}	7.60×10^{-5}
2	1.75×10^{-4}	3.88	2.43×10^{-5}	1.51×10^{-4}
3	2.6×10^{-4}	5.52	3.45×10^{-5}	2.25×10^{-4}
4 & 5	4.27×10^{-4}	9.62	6.1×10^{-5}	3.66×10^{-4}
6 & 7	6.03×10^{-4}	13.22	1.01×10^{-4}	5.02×10^{-4}
8 & 9	7.78×10^{-4}	16.79	$1\ 05 \times 10^{-4}$	6.73×10^{-4}
	Extrapolation	18.33		$7.15 \pm 0.05 \times 10^{-4}$

By extrapolation to 18.33 mm., the vapor pressure of water at 20.89°, the curve shown in Fig. 4 indicates that 7.15×10^{-4} mole of water is required to saturate 25.635 cc. of benzene. When this, saturation value is interpreted in grams, the figure reduces to 0.00057 g. of water per gram of benzene, or 0.057%, which checks the value given in the "International Critical Tables."

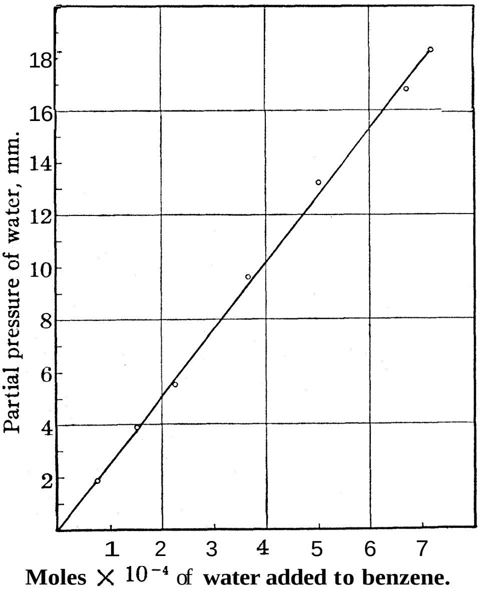

Fig. 4.

From the experimental data presented in Table II and in Fig. 4, it is evident that the solution of water in benzene follows Henry's law rigidly but not Raoult's law. However, the results for benzene at the saturation value and below may be expressed by the equation

$$P = \frac{x}{x_{\text{satd.}}} P_{\text{satd.}} \text{ at constant temperature}$$

where x is mole fraction of water present and $x_{\text{satd.}}$ is mole fraction of water required to saturate the benzene. The average deviation of the observed pressures from this relation is 0.19 mm. pressure or 2.28% of the calculated value.

It seems reasonable to expect that this relation would be fundamental for solutions of water in carbon tetrachloride and carbon disulfide, or for solutions of any two other mutually very insoluble liquids.

In conclusion, the author wishes to express her sincere appreciation to Dr. W. A. Patrick, under whose guidance this problem was completed, and to Dr. J. C. W. Frazer, who in conjunction with Dr. Patrick suggested and cooperated in the investigation.

Summary

1. Benzene free from impurities does not impart color to pure phosphorus pentoxide nor does it form such addition compounds with phosphorus as were described by Giran.
2. Methods have been found that produce benzene free from the usual sulfur compounds of which carbon disulfide has been found to be as undesirable as thiophene, though it is more commonly ignored than the latter.
3. Benzene that has been dried with phosphorus pentoxide in *a* fused glass apparatus for three years has not shown any change in vapor pressure with respect to the normal liquid in the same apparatus.
4. Within twenty-four hours, benzene, carbon tetrachloride and carbon disulfide dried with activated silica gel manifested vapor pressure differences or decreases, as compared with the normal liquids, that were finally comparable in magnitude and direction with those reported by other investigators in the field of intensive drying.
5. Experimental evidence has been submitted and discussed to support the theory that the vapor pressure decreases or differences from the normal may be explained by assuming the presence of minute traces of water vapor in the normal liquid rather than any catalytic effect due to the removal of water from the dried liquid.
6. Calculations from solubility data show that only 0.000229 g. of water is required to produce a partial pressure of 7 mm. of water in one gram of benzene at 20°. This value deviates from Raoult's law, which requires 405 times more water than is actually effective.
7. The partial pressures of solutions of water in benzene at 20.89° have been measured and plotted. Extrapolation of the curve gives a value of the solubility of water in benzene at 20° which checks that given in "International Critical Tables."
8. The relation of the partial pressures to mole fractions in solutions of water in benzene may be expressed by the equation $P = (x/x_{\text{satd.}})P_{\text{satd.}}$.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY, AND THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

THE SYSTEM Na_2SO_4–NaF–NaCl–H_2O. I. THE TERNARY SYSTEMS WITH WATER AND TWO SALTS[1]

BY H. W. FOOTE AND J. F. SCHAIRER

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Before investigating equilibrium relations in the quaternary system Na_2SO_4–NaF–NaCl–H_2O, it was necessary to determine first these relations in each of the three ternary systems of two salts and water. The data for the ternary systems are given here and the data for the quaternary system will be published in Part II.

Sodium sulfate and sodium chloride were purified by the usual methods. Sodium fluoride forms an acid fluoride in the presence of only a small excess of hpdrofluoric acid.[2] To obtain pure sodium fluoride, recrystallized sodium carbonate was dissolved in a small volume of water and neutralized with the smallest possible excess of hydrofluoric acid. After warming to remove carbon dioxide, the solution was cooled and the precipitated sodium fluoride filtered and washed with alcohol. An analysis by conversion to the sulfate and an optical examination with the petrographic microscope checked its purity.

For the determination of solubility isotherms appropriate mixtures of salts and water were placed in hard rubber bottles and shaken at constant temperature in a water thermostat for at least twenty-four hours. A check upon the attainment of equilibrium was made by running duplicate determinations held at constant temperature for longer periods of time. Solutions for analysis were removed through filters of glass wool directly into weighing tubes. Depending on the solid phases present and whether a wet or dry residue was desired, different procedures were followed. The solid phases, or "residues," which were in equilibrium with the solutions, were either pressed between filter papers until dry, or washed quickly with alcohol on a Gooch crucible and then dried between filter papers. Both methods have disadvantages, and in general it is not possible to obtain the composition of the residues as accurately as that of the solutions. In some cases wet residues were analyzed and the composition of the solids determined by the graphic method of Schreinemakers.[3]

In the analysis of solutions and solids, sodium chloride was determined by titration with silver nitrate solution, using potassium chromate as the indicator. The determination of sulfate as $BaSO_4$ is entirely unreliable in

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[1] The data presented in this paper constitute a portion of a Dissertation presented to the Graduate School of Yale University by J. F. Schairer, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1928.

[2] Jehu and Hudleston, J. Chem. *Soc.*, **125**, 1451–1456 **(1924).**

[3] Schreinemakers, *Z. physik.* Chem., **43**, 307 (1903).

the presence of fluorides. Sodium fluoride was determined by converting the salts to sodium sulfate with sulfuric acid and igniting in a current of air containing ammonia, and sodium sulfate determined by difference. On account of the considerable difference between the equivalent weights of sodium fluoride and sodium sulfate, this method of indirect analysis is much more accurate than is commonly the case with indirect methods. The formula used in calculating the weight of sodium fluoride is: $x = 1.4468 (b - a) - 0.3113 c$, in which a, b and c represent, respectively, the weight of mixed salts, the weight of sodium sulfate after the conversion of chlorides and fluorides to sulfate, and the weight of sodium chloride.

Eutectic points with ice as one of the solid phases were determined in a small vacuum-jacketed flask, by shaking a mixture of wet crushed ice with an excess of the salt or salts in question. After removal of a sample of the solution for analysis, more of each solid phase was added and the temperature again observed. The thermometers were calibrated with care and the eutectic temperatures are probably in error by not more than 0.1'. Transition temperatures were determined by the same general method as eutectic temperatures.

The System Na_2SO_4–NaF–H_2O.—In the system Na_2SO_4–NaF–H_2O a double salt $Na_2SO_4 \cdot NaF$ forms. Wolters[4] found this double salt at high temperatures in his investigation of the fusion relations in the ternary system Na_2SO_4–NaF–NaCl. Below a transition temperature (17.5') the double salt breaks down into sodium fluoride and the decahydrate of sodium sulfate. Above the transition temperature of sodium sulfate (32.38°), a solubility isotherm consists of three branches meeting in two univariant points at which two solid phases (sodium fluoride and double salt or sodium sulfate and double salt) are in equilibrium. The transition temperature of sodium sulfate decahydrate in the presence of the double salt (32.36') is almost identical with that of the pure decahydrate, on account of the slight solubility of sodium fluoride. Between 32.36° and the transition point of the double salt (17.5°), a solubility isotherm consists of three branches, with sodium sulfate present as the decahydrate. Below 17.5°, an isotherm consists of two branches meeting at a point where the two single salts coexist as solid phases. The solubility data obtained at four temperatures are given in Table I. Where less than 0.1% of a salt was found in solution it is reported as a trace (tr.).

The solid phases present in the residue were determined in the usual manner by plotting the composition of solutions and residues on an equilateral triangle. The nature of the solid phases was checked by an examination with the petrographic microscope. The identity of the solid phase or phases in equilibrium with a given solution is noted in Table I. Ds indicates the double salt $Na_2SO_4 \cdot NaF$.

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[4] Wolters, *Neues Jahrb. Mineral. Geol. Beil.*, 30, 55–96 (1910).

TABLE I

SOLUBILITY ISOTHERMS—SYSTEM Na_2SO_4–NaF–H_2O

Solution,		Residue,		
% Na_2SO_4	% NaF	% Na_2SO_4	% NaF	Solid phases
		T = 35°		
32.97	None			Na_2SO_4
32.96	None			Na_2SO_4
32.87	Tr.	95.43	4.57	Na_2SO_4 and Ds[b]
32.75	0.13	87.97	12.03	Na_2SO_4 and Ds
32.79	Tr.	82.35	17.65	Na_2SO_4 and Ds
18.11	0.62	64.57	18.51"	Ds[b]
11.60	1.57	77.23	22.77	Ds
9.58	2.09	75.68	24.32	Ds
8.51	2.45	65.48	34.52	Ds and NaF
8.73	2.54	8.43	91.56	Ds and NaF
4.34	3.18	1.61	74.18"	NaF
None	4.02			NaF
None	3.97			NaF
		T = 25°		
21.71	None			$Na_2SO_4\cdot10H_2O$
21.71	None			$Na_2SO_4\cdot10H_2O$
21.25	0.42	43.93	1.40"	$Na_2SO_4\cdot10H_2O$ and Ds
21.43	0.33	55.91	13.17"	$Na_2SO_4\cdot10H_2O$ and Ds
11.48	1.74	76.75	23.25	Ds
8.86	2.37	46.88	28.89"	Ds and NaF
8.48	2.34	14.49	43.60"	Ds and NaF
4.48	3.13	2.17	57.79"	NaF
None	3.98			NaF
None	3.97			NaF
		T = 15°		
11.72	None			$Na_2SO_4\cdot10H_2O$
11.67	None			$Na_2SO_4\cdot10H_2O$
9.48	2.51	39.07	3.94"	$Na_2SO_4\cdot10H_2O$ and NaF
9.51	2.48	11.88	69.50"	$Na_2SO_4\cdot10H_2O$ and NaF
None	3.93			NaF
None	3.92			NaF
		T = 10°		
8.31	None			$Na_2SO_4\cdot10H_2O$
8.38	None			$Na_2SO_4\cdot10H_2O$
6.41	2.92	13.25	53.14"	$Na_2SO_4\cdot10H_2O$ and NaF
6.37	3.04	36.59	4.21"	$Na_2SO_4\cdot10H_2O$ and NaF
3.95	3.20	1.96	55.53"	NaF
None	3.92			NaF
None	3.97			NaF

[a] Wet residue analyzed. [b] Ds = $Na_2SO_4\cdot NaF$ (double salt).

The data for eutectic and transition temperatures are given in Table II. The two eutectics with ice and a single salt have been determined before.[5]

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[5] Guthrie, *Phil. Mag.*, **6**, 40 (1878); De Coppet, Z. *physik. Chem.*, 22, 239 (1897); Chretien. *Caliche*, 9, 248 (1927).

The transition point where the solid phases are $Na_2SO_4\cdot 10H_2O$, NaF and $Na_2SO_4\cdot NaF$ is somewhat difficult to obtain. Solubility isotherms indicated that this transition temperature was between 15 and 25°. A mixture of sodium fluoride, decahydrate of sodium sulfate and a small amount of the double salt $Na_2SO_4\cdot NaF$ and water was placed in a vacuum flask at 21° and the temperature observed. The temperature slowly dropped, finally remaining constant for several hours. The reverse of this determination, starting below the transition temperature, did not give a sharp result.

TABLE II

EUTECTIC AND TRANSITION TEMPERATURES—SYSTEM Na_2SO_4–NaF–H_2O

Solid phases	Temp., °C.	Solution % Na_2SO_4	Solution % NaF	Corresponding point in the diagram (Fig, 1)
Ice + NaF	−3.02	None	4.02	A
Ice + NaF	−2.98	None	3.82	A
Ice + $Na_2SO_4\cdot 10H_2O$	−1.11	3.97	None	B
Ice + $Na_2SO_4\cdot 10H_2O$	−1.14	4.11	None	B
Ice + NaF + $Na_2SO_4\cdot 10H_2O$	−3.08	1.65	3.60	C
Ice + NaF + $Na_2SO_4\cdot 10H_2O$	−3.08	1.70	3 34	C
Ice + NaF + $Na_2SO_4\cdot 10H_2O$	−3.00	1.68	3.33	C
$Na_2SO_4\cdot 10H_2O$ + NaF + Ds	17.45	12.54	2.00	D
$Na_2SO_4\cdot 10H_2O$ + NaF + Ds	17.50	12.63	1.83	D
$Na_2SO_4\cdot 10H_2O$ + Na_2SO_4[a]	32.383"	33.24[b]	None	E
$Na_2SO_4\cdot 10H_2O$ + Na_2SO_4 + Ds	32.36	33.16	Tr	F
$Na_2SO_4\cdot 10H_2O$ + Na_2SO_4 + Ds	32.36	33.06	Tr.	F

[a] "International Critical Tables," 1926, Vol. I, p. 66. [b] *Ibid.*, 1928, Vol. III, p. 371.

These data cannot be properly shown as a projection on a triangular base. The results are, therefore, represented in a space figure (Fig. 1),

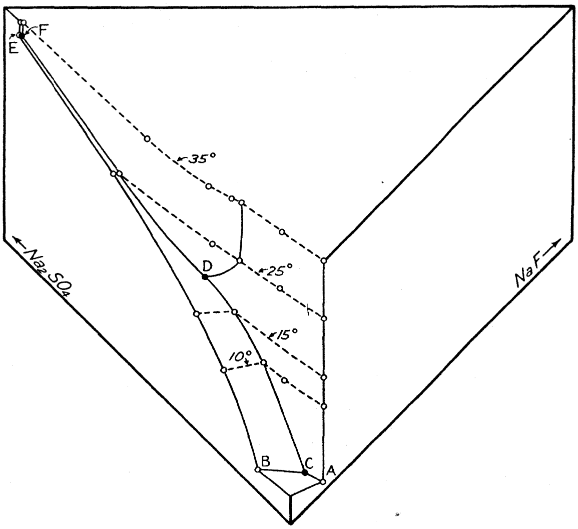

Fig. 1.—System Na_2SO_4–NaF–H_2O. Space model.

plotting temperatures vertically from a triangular base. The eutectic and transition temperatures (Fig. 1) are lettered to correspond with the data in Table II. Solubility isotherms are represented as dotted lines. The results given in the tables for invariant and univariant points have been averaged for representation in Fig. 1.

The Double Salt $Na_2SO_4 \cdot NaF$.—The double salt $Na_2SO_4 \cdot NaF$ was first described by Marignac[6] who obtained it by evaporation of the mother liquor from a preparation of sodium fluoride with hydrofluoric acid containing some sulfuric acid. He describes it as occurring in hexagonal plates twinned parallel to the base. The crystals were a combination of the base and four rhombohedrons. The crystals gave poor signals on the goniometer. Marignac assigns the crystals with some doubt to the rhombohedral class of the hexagonal system.

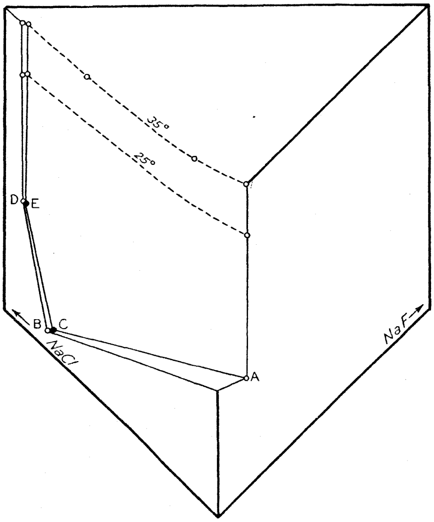

Fig. 2.—System NaF–NaCl–H_2O. Space model.

Wolters[7] prepared the double salt from water solution at 35° and claims that it is pseudo-hexagonal up to 105° (±2°), where it becomes hexagonal. This transition temperature is above the range of temperatures studied by us.

Crystals of the double salt were prepared by isothermal evaporation at 35°. Five crystals were measured on a two circle goniometer. The crystals appeared bright and sharp but did not give good signals. The crystals are tabular with hexagonal outline and decided trigonal symmetry. The base is rough and the other faces, although very definite, usually gave many goniometric signals in the zone with the base. Twinning on the base is common. The results of our measurements on five crystals give

$$c = 1.77$$
$$(0001) \wedge (10\bar{1}1) = 63.9°; \quad (0001) \wedge (01\bar{1}2) = 45.7°$$
$$(0001) \wedge (03\bar{3}2) = 72.0°$$

The double salt $Na_2SO_4.NaF$ is uniaxial, optically positive, $\epsilon_{Na} = 1.430$, $\omega_{Na} = 1.436$ with a cleavage parallel to (0001).

The System NaF–NaCl–H_2O.—The solubility isotherms at 25 and 35°, taken in connection with the composition of the residues, show that no double salt forms and that solid solution, if present, is too slight to be

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[6] Marignac, *Annales des Mines*, *15*, 236 (1859).

[7] Ref. 4.

detected. The transition temperature of sodium chloride dihydrate has been determined repeatedly by others, though the results in the literature do not agree closely. We found it sharp and easily obtained. Sodium fluoride lowers this transition temperature but slightly on account of its slight solubility in the presence of sodium chloride.

The results obtained are given in Tables III and IV and are represented in Fig. 2.

TABLE III

SOLUBILITY ISOTHERMS—SYSTEM NaCl–NaF–H_2O

Solution		Residue		
% NaCl	% NaF	% NaCl	% NaF	Solid phases
		T = 35°		
26.63	None			NaCl
26.61	None			NaCl
26.18	0.34	74 77	25.23	NaCl and NaF
26.13	0.29	23.85	76.15	NaCl and NaF
18.43	0.54	4.58	75.98"	NaF
5.41	2.38	1 58	72 94[a]	NaF
None	4.02			NaF
None	3.97			NaF
		T = 25°		
26.43	None			NaCl
26.38	None			NaCl
26.12	0 31	56.50	25.91"	NaCl and NaF
26.24	.12	19.58	42.06"	NaCl and NaF
None	3 98			NaF
None	3.97			NaF

[a] Wet residue analyzed.

TABLE IV

EUTECTIC AND TRANSITION TEMPERATURES—SYSTEM NaCl–NaF–H_2O

		Solution		Corresponding point in diagram
Solid phases	Temp., °C.	% NaCl	% NaF	(Fig. 2)
Ice + NaF	− 3.02	None	4.02	A
Ice + NaF	− 2.98	None	3.82	A
Ice + NaCl·$2H_2O$	−20.94	23.18	None	B
Ice + NaCl·$2H_2O$ + NaF	−21.19	23.69"	0.24	C
NaCl·$2H_2O$ + NaCl	+ 0.08	26.39	None	D
NaCl·$2H_2O$ + NaCl	.10	26.53	None	D
NaCl·$2H_2O$ + NaCl + NaF	− .06	26.25	0.19	E

[a] This result is probably somewhat too high.

The System Na_2SO_4–NaCl–H_2O.—This system has been investigated previously by Meyerhoffer and Saunders,[8] Seidell and Blasdale.[10] We have determined the points necessary for use in the four-component sys-

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[8] Meyerhoffer and Saunders, *Z. physik. Chem.*, 28, 453 (1899).

[9] Seidell, *Am. Chem. J.*, 27, 55 (1902).

[10] Blasdale, *Ind. Eng. Chem.*, 10, 344 (1918).

tem. So far as they are comparable, our results check closely with those of Blasdale.

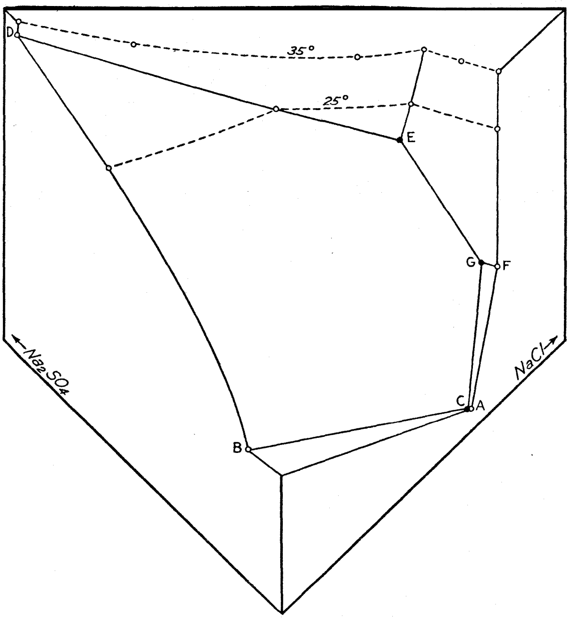

Fig. 3.—System Na_2SO_4–NaCl–H_2O. Space model.

The results obtained are given in Tables V and VI and are plotted in Fig. 3 in the same manner as the preceding ternary systems.

TABLE V

SOLUBILITY ISOTHERMS—SYSTEM Na_2SO_4–NaCl–H_2O

Solution		Residue		
% Na_2SO_4	% NaCl	% Na_2SO_4	% NaCl	Solid phases
		T = 35°		
82.97	None			Na_2SO_4
32.96	None			Na_2SO_4
24.43	5.86	100.00	None	Na_2SO_4
9.78	18.61	98.67	1.33"	Na_2SO_4
6.00	23.43	75.50	24.50	Na_2SO_4 and NaCl
6.17	23.39	20.78	79.22	Na_2SO_4 and NaCl
6.11	23.41	1.77	98.23	Na_2SO_4 and NaCl
3.00	25.01	None	100.00	NaCl
None	26.63			NaCl
None	26.61			NaCl
		T = 25°		
21.71	None			$Na_2SO_4 \cdot 10H_2O$
21.71	None			$Na_2SO_4 \cdot 10H_2O$
14.98	14.15	78.25	1.94[b]	$Na_2SO_4 \cdot 10H_2O$ and Na_2SO_4
15.01	14.06	65.58	1.65"	$Na_2SO_4 \cdot 10H_2O$ and Na_2SO_4

TABLE V (Concluded)

Solution		Residue		
% Na_2SO_4	% NaCl	% Na_2SO_4	% NaCl	Solid phases
14.91	14.10	64.70	1.68[b]	$Na_2SO_4 \cdot 10H_2O$ and Na_2SO_4
14.84	14.17	46.39	2.29[b]	$Na_2SO_4 \cdot 10H_2O$ and Na_2SO_4
6.91	22.78	72.84	16.21[b]	Na_2SO_4 and NaCl
6.92	22.76	12.61	72.54[b]	Na_2SO_4 and NaCl
None	26.63			NaCl
None	26.61			NaCl

[a] This residue was contaminated with sodium chloride from the solution. [b] Wet residue.

TABLE VI

EUTECTIC AND TRANSITION TEMPERATURES—SYSTEM Na_2SO_4–NaCl–H_2O

		Solution		
Solid phases	Temp., °C.	% Na_2SO_4	% NaCl	Corresponding point in diagram (Fig. 3)
Ice + $NaCl \cdot 2H_2O$	−20.94	None	23.18	A
Ice + $Na_2SO_4 \cdot 10H_2O$	− 1.11	3.97	None	B
Ice + $Na_2SO_4 \cdot 10H_2O$	− 1.14	4.11	None	B
Ice + $Na_2SO_4 \cdot 10H_2O$ + $NaCl \cdot 2H_2O$	−21.32	0.31	23.43	C
Na_2SO_4 + $Na_2SO_4 \cdot 10H_2O$[a]	32.383[a]	33.24[b]	None	D
Na_2SO_4 + $Na_2SO_4 \cdot 10H_2O$ + NaCl	17.90	7.77	22.31	E
$NaCl \cdot 2H_2O$ + NaCl	+ 0 08	None	26.39	F
$NaCl \cdot 2H_2O$ + NaCl	+ 10	None	26.53	F
$NaCl \cdot 2H_2O$ + NaCl + $Na_2SO_4 \cdot 10H_2O$	.0	1.32	25.79	G

[a] "International Critical Tables," **1926**, Vol. I, p. 66. [b] *Ibid.*, **1928**, Vol. 111, p. 371.

Summary

Solubility determinations were made on the ternary system Na_2SO_4–NaF–H_2O at 35, 25, 15 and 10°, and on the ternary systems NaF–NaCl–H_2O and Na_2SO_4–NaCl–H_2O at 35 and 25°. The necessary eutectics and transition temperatures were determined to define each ternary system between its ternary eutectic and 35°. These data are presented by tables and graphically by space models.

The nature and identity of the various solid phases was checked with the petrographic microscope. The crystallographic and optical properties of the double salt $Na_2SO_4 \cdot NaF$ were measured.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY, AND THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

THE SYSTEM Na_2SO_4–NaF–NaCl–H_2O. II. THE QUATERNARY SYSTEM AT 25 AND 35°[1]

BY H. W. FOOTE AND J. F. SCHAIRER

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The quaternary system Na_2SO_4–NaF–NaCl–H_2O is derived from three ternary systems, each composed of two of the above salts and water. The data on these three systems were presented in the first part of this paper.[2] At a given temperature, proceeding from each univariant point in these systems, where two solid phases coexist, there is a solubility curve ending at a point where a third solid phase appears. We have determined the solubility relations and the solid phases for the quaternary system at the temperatures 25 and 35°.

The chief experimental difficulty in the investigation was to obtain the gross composition of the residues, because it is impossible to free them entirely from solution. At 35°, since all the solids are anhydrous, it was possible to filter the solids rapidly on a warmed Gooch crucible, after removing a sample of the solution for analysis. The solids were washed quickly with alcohol and dried between filter papers. At 25°, except where noted, we analyzed wet residues. Since the composition of the solution is known, the gross composition of the solid residues may be calculated.[3] By making a sufficient number of such determinations, it is possible to decide whether one is at a univariant point (with three solid phases and constant solubility) or on a divariant curve (with two solid phases and varying solubility). We made use of the optical properties of the crystals to determine qualitatively the number and kind of solid phases as a check on the analytical data.

The results are given in Table I. The composition of the residue free from mother liquor is given in all cases, whether determined directly by analysis or calculated after analysis of solution and wet residue. Sodium fluoride is only slightly soluble in the more concentrated solutions of sodium sulfate and chloride. Whenever less than 0.1% was found, it is reported as a trace.

To show the results in a diagram, we have plotted the solubilities of the three salts along three axes which make an angle of 120° with each other. In ternary systems it is convenient to represent isotherms in an equilateral triangle in which composition of both solutions and residues may be plotted.

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[1] The data presented in this paper constitute a portion of a Dissertation presented to the Graduate School of Yale University by J. F. Schairer, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1928.

[2] Poote and Schairer, THIS JOURNAL, 52, 4202 (1930).

[3] This method can be used only when the solid phases do not contain all four components.

Table I

Solubility Isotherms—System Na_2SO_4–NaF–NaCl–H_2O

	Solution			Residue			
No.	% Na_2SO_4	% NaF	% NaCl	% Na_2SO_4	% NaF	% NaCl	Solid phases
				$T = 35°$			
1	6.14	Tr.	23.37	65.39	0.96	33.65	Na_2SO_4 + NaCl + Ds[a]
2	5.95	Tr.	23.54	71.03	668	22.29	Na_2SO_4 + NaCl + Ds
3	0.49	0.12	26.08	45.88	15.21	38.91	NaF + NaCl + Ds
4	.41	.30	26.03	10.68	16.88	72.44	NaF + NaCl + Ds
5	.17	.31	26.18	14.77	74.31	10.92	NaF + NaCl + Ds
6	.24	.43	22.36	4511	53.89	1.00	NaF + Ds
7	.80	.49	21.05	70.33	27.37	2.30	NaF + Ds
8	1.43	.80	16.14	56.52	43.21	0.27	NaF + Ds
9	2.67	1.27	10.71	61.77	38.23	None	NaF + Ds
10	4.84	1.80	5.42	68.42	31.58	None	NaF + Ds
11	6.89	Tr.	22.31	86.27	10.02	3.71	Na_2SO_4 + Ds
12	8.73	0.35	19.47	87.46	7.66	4.88	Na_2SO_4 + Ds
13	14.13	0.62	13.60	85.15	13.37	1.48	Na_2SO_4 + Ds
14	21.39	Tr.	8.09	85.70	13.46	0.84	Na_2SO_4 + Ds
15	3.66	0.46	24.32	57.55	13.71	28.69	NaCl + Ds
16	322	.14	24.81	53.48	13.50	33.02	NaCl + Ds
17	20.83	.23	4.93	79.39	20.59	None	Ds
18	17.66	.13	8.55	79.48	20.52	None	Ds
19	7.46	.75	7.26	77.78	22.22	None	Ds
20	5.08	.24	14.59	77.68	22.32	None	Ds
21	4.35	0.19	18.57	77.02	22.67	0.31	Ds
22	8.17	Tr.	18.38	76.70	20.76	2.53	Ds
23	2 97	0.20	23.36	75.37	21.02	3.61	Ds
24	4.39	0 61	21.64	75.51	18.48	6.01	Ds
25	1.51	Tr.	23.34	74.68	19.03	6.29	Ds
				$T = 25°$			
1	0.21	0.43	25.96	11.98	11.30	76.72	NaF+NaCl+Ds[a]
2	0.50	0.23	25.93	56.51	21.48	22.01	NaF + NaCl + Ds
3	0.43	0.27	25.90	11.27	74.00	14.73	NaF + NaCl + Ds
4	7.04	Tr.	22.71	66.56	12 25	21.19	Na_2SO_4 + NaCl + Ds
5	6.82	0.10	22.77	19.43	2.98	77.59	Na_2SO_4 + NaCl + Ds
6	6.98	Tr.	22.73	86.75	2.87	10.38	Na_2SO_4 + NaCl + Ds
7	14.75	Tr.	13.79	66.25[b]	3.98	None	Na_2SO_4 + $Na_2SO_4 \cdot 10H_2O$ + Ds
8	14.76	Tr.	13.78	76.92[b]	20.41	None	Na_2SO_4 + $Na_2SO_4 \cdot 10H_2O$ + Ds
9	5.23	Tr.	23.61	43.84	10.95	45.21	NaCl + Ds
10	9.72	Tr.	19.29	90.41	7.57	2 02	Na_2SO_4 + Ds
11	4.35	0.60	21.48	77.64	21.67	0.69	Ds
12	4.47	Tr.	18.41	77.31	22.69	None	Ds
13	4.60	0.77	14.35	76.85	23.15	None	Ds
14	7.71	0.69	6.98	77.17	22.83	None	Ds

[a] Ds = double salt $Na_2SO_4 \cdot NaF$. (This is capable of taking up a limited amount of NaCl in solid solution which replaces an equivalent quantity of NaF. The pure double salt contains 77.18% Na_2SO_4.)

[b] This residue was air dried for analysis. The others were analyzed wet and the composition of the dried residues, as given in the table, was calculated.

However, in a quaternary system, it is not feasible to represent the composition of both solutions and residues by a single diagram. We have therefore represented the composition of residues by means of a separate triangular diagram used in conjunction with the solubility diagram to show the relations of residues to their solutions. This is entirely satisfactory when the residues are anhydrous, which is the case at 35°. At 25° this method of representing residues cannot be used, as both anhydrous Na_2SO_4 and $Na_2SO_4 \cdot 10H_2O$ are present.

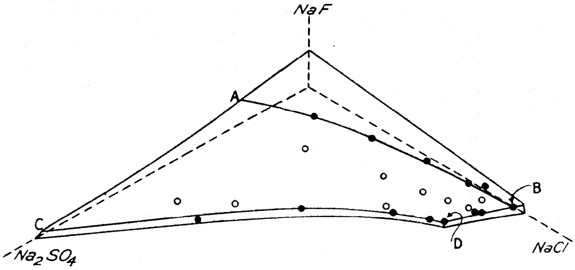

Fig. 1.—System Na_2SO_4–NaF–NaCl–H_2O. Solubility isotherm at 35°.

The solubility data are plotted in Figs. 1 (35° isotherm) and 2 (25° isotherm). At univariant points, the average result of the several determinations is represented. Some univariant points taken from the ternary systems have been displaced outward slightly to make the diagram clear, since they almost coincide with the corresponding quaternary points.

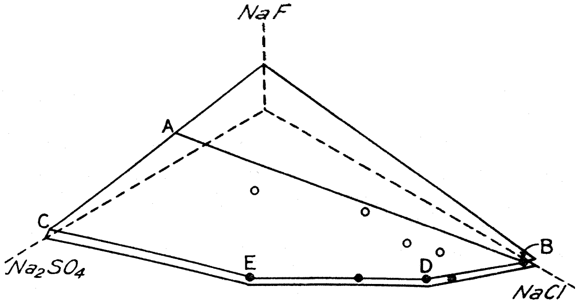

Fig. 2.—System Na_2SO_4–NaF–NaCl–H_2O. Solubility isotherm at 25°.

At 35° (Fig. 1) the double salt (in which some NaCl replaces NaF) is stable throughout the area ABDC. The solubility results obtained in this area (Nos. 17–25 in Table I) are plotted as circles. At the univariant points B and D, three solid phases coexist in equilibrium with solution. Univariant points and points on the three curves are plotted as black dots. At 25° (Fig. 2), the relations are similar but an additional univariant point E exists, where the solid phases are double salt, Na_2SO_4 and $Na_2SO_4 \cdot 10H_2O$.

At this point the double salt contains no appreciable amount of NaCl. Only a few determinations were made at 25°, since the general relations were already clear.

The residues at 35°, so far as they contain all three salts, are plotted in Fig. 3. In considering this diagram, it must be remembered that the double salt can take up a limited amount of chloride in solid solution, which replaces an equivalent amount of fluoride. This replacement only becomes appreciable in the presence of considerable amounts of sodium chloride in solution. (Nos. 22–25 of Table I.) The composition of the double salt is therefore variable and represented by the line ABC. The maximum amount of solid solution, represented by C, is not accurately known, but is undoubtedly a function of temperature. The solution yielding the maximum is very probably at the univariant point where the solid phases are Na_2SO_4, NaCl and double salt. In the table of data at 35° (Table I), Nos. 17–21 contain little or no chloride in the double salt and their composition falls very close to the point A of Fig. 3. The other residues consisting of double salt showing appreciable solid solution (Nos. 22–25, Table I) are plotted. Two of them are somewhat off the line AC, showing that these were slightly contaminated with sodium chloride from the solution, though their solubility shows quite definitely that but a single phase was present. The areas ACD, ABE and BCF (Fig. 3) correspond to mixtures of Na_2SO_4 with double salt, NaF with double salt and NaCl with double salt, respectively. The numbered points refer to the numbers in Table I at 35°.

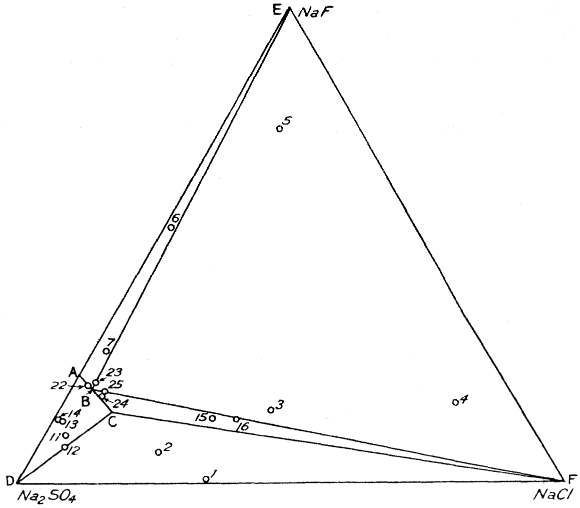

Fig. 3.—Composition of solid phases in equilibrium with solutions at 35°.

The residues in equilibrium with solutions at 25° show the same general relations. Complete representation of the residues on an equilateral triangle is not possible because anhydrous Na_2SO_4 and $Na_2SO_4 \cdot 10H_2O$ are present in some mixtures.

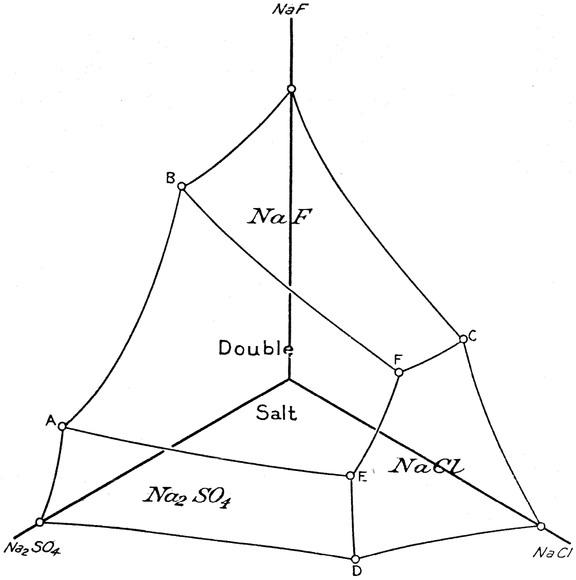

Fig. 4.—Hypothetical quaternary isotherm assuming that no triple salt appears.

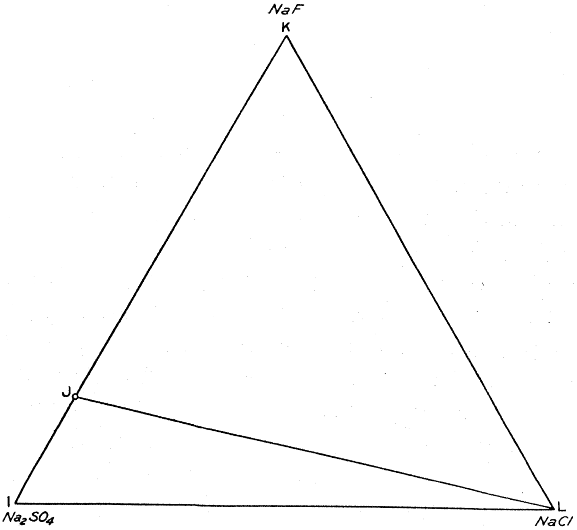

Fig. 5.—Composition of solid phases in equilibrium with solutions of Fig. 4.

There was a strong probability at the outset of the work that the mineral sulfohalite ($2Na_2SO_4 \cdot NaCl \cdot NaF$) might appear as one of the solid phases at the temperatures investigated. If this had appeared, it should be one of the solid phases in a portion of the area ABDC (Fig. 1). Then at the point B and possibly at D it would be one of the three solid phases. There would also be two other univariant points each with three solid phases and the corresponding divariant curves. It can be shown by considering the relation between solutions and residues that the solid phase $2Na_2SO_4 \cdot NaCl \cdot NaF$ did not appear at the temperatures investigated and that the solid phase in the area ABDC (Figs. 1 and 2) of the two investigated isotherms is not pure double salt $Na_2SO_4 \cdot NaF$ but a solid solution in which a limited part of the fluoride is replaced by chloride.

Let us assume that no triple salt appears in the quaternary system and that only the double salt $Na_2SO_4 \cdot NaF$ (with no solid solution) and the three single salts appear. Then the hypothetical solubility relations at some constant temperature are represented diagrammatically in Fig. 4. The assumed values for solubilities used to prepare Fig. 4 were so chosen as to prevent crowding of lines and points for clarity in presentation. Then the residues in equilibrium with such solutions may be shown on an equilateral triangle, Fig. 5. J represents the composition $Na_2SO_4 \cdot NaF$. If the assumed solubility relations were correct, all residues whose composition lay in the area IJL (Fig. 5) should have the same solubility (represented by E of Fig. 4) and similarly all those in the area JKL (Fig. 5) should have the solubility represented by F (Fig. 4).

By examining the actual data given in Table I and presented graphically in Figs. 1, 2 and 3, we find that the experimental data do not fit the assumption we have made.

If we assume that a triple salt $2Na_2SO_4 \cdot NaCl \cdot NaF$ appears and that the other solid phases in the quaternary system are pure double salt $Na_2SO_4 \cdot NaF$ and the single salts, these hypothetical relations can be shown diagrammatically in Fig. 6 (assumed values chosen to prevent crowding in the figure). The composition of all residues may be shown in Fig. 7. J represents the composition $Na_2SO_4 \cdot NaF$ and M the composition $2Na_2SO_4 \cdot NaCl \cdot NaF$. If the assumed solubility relations were correct, all residues whose composition lay in the areas IJM, JMK, MKL and IML (Fig. 7), respectively, would have the solubilities H, G, F and E (Fig. 6), respectively.

Again, examining the actual data given in Table I and presented graphically in Figs. 1, 2 and 3, we find that the experimental data are not in accord with the assumption made.

The experimental data show that at the temperatures investigated no triple salt forms and that in the quaternary system the double salt $Na_2SO_4 \cdot NaF$ has a limited part of its fluoride replaced by chloride. This fact was confirmed by microscopic examination. The replacement of fluoride by chloride raises the indices of refraction of the double salt.

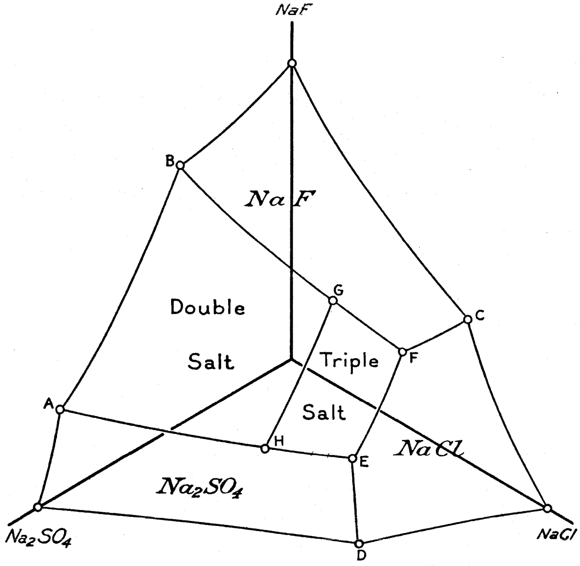

Fig. 6.—Hypothetical quaternary isotherm assuming existence of a triple salt $2Na_2SO_4 \cdot NaF \cdot NaCl$.

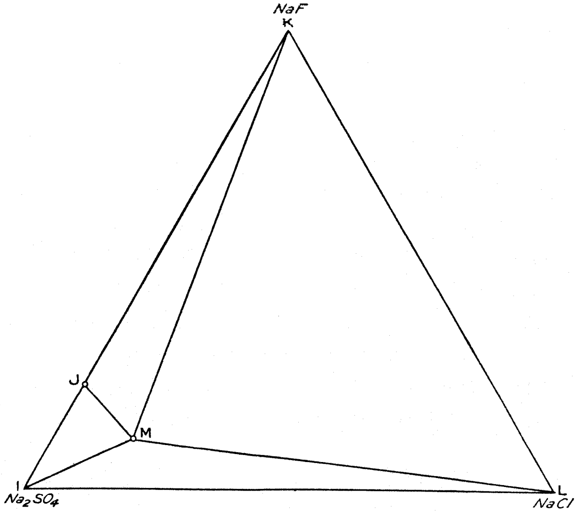

Fig. 7.—Composition of solid phases in equilibrium with solutions of Fig. 6.

In two cases after equilibrium had been reached at the points B and D (Figs. 1 and 2), we introduced a small amount of the natural mineral (sulfohalite $2Na_2SO_4 \cdot NaF \cdot NaCl$ from Searles Lake, California) into the equilibrium bottles, which were again shaken at constant temperature. This was done to overcome any possible metastable condition and was without effect on the solubility or nature of solid phases present.

Sulfohalite.—We obtained several small crystals of the natural mineral, sulfohalite, from the U. S. National Museum (Museum No. 93,659). These crystals from Searles Lake, California, all proved quite unsuitable for chemical study owing to the very numerous and well distributed tiny laths and grains of an impurity. The sulfohalite crystals were sharp octahedrons, optically isotropic, $n_{Na} = 1.454$. Sulfohalite is undoubtedly a distinct mineral. It is well crystallized and optically distinct from all other mineral species. Both Penfield[4] and Gale and Hicks[5] give its composition as $2Na_2SO_4 \cdot NaF \cdot NaCl$. It might be supposed that the mineral represented an extreme case of solid solution in which the replacement of fluoride by chloride was by chance 1:1. The mineral, however, is isometric while the solid solution is hexagonal rhombohedral. It seems very unlikely that sulfohalite might appear at a transition temperature above 35°, since Teeple[6] has shown that the brine which permeates the entire salt deposit at Searles Lake is uniformly at 23° throughout the year. Our isotherms show no indication of the mineral between 25 and 35°. If it exists in stable equilibrium, it is likely that this can only be the case below 25°, which can be determined by further isotherms at lower temperatures.

Summary

Solubility isotherms for the quaternary system Na_2SO_4–NaF–NaCl–H_2O have been determined at 25 and 35°. At these temperatures, the double salt $Na_2SO_4 \cdot NaF$ forms a solid solution in which fluoride is replaced by chloride to a limited extent.

No indication of the mineral sulfohalite $2Na_2SO_4 \cdot NaF \cdot NaCl$ has been obtained at these temperatures.

A graphic method has been developed to show the relation of the composition of anhydrous solid phases to the solutions in equilibrium with such phases in quaternary systems composed of water with three salts containing a common ion.

New optical and crystallographic data are recorded for the compound $Na_2SO_4 \cdot NaF$.

WASHINGTON, D. C.

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[4] Penfield, *Am. J. Sci.*, *9*, 425 (1900).

[5] Gale and Hicks, *ibid.*, 38, 273 (1914).

[6] Teeple, *Ind. Eng. Chem.*, *13*, 249 (1921).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE BAVARIAN ACADEMY OF SCIENCES, DIVISION OF PHYSICAL CHEMISTRY]

THE HEATS OF DILUTION OF POTASSIUM CHLORIDE IN SUCROSE AND UREA SOLUTIONS AS SOLVENTS BELOW 0.1 M AT 25°[1]

BY E. LANGE AND A. L. ROBINSON

RECEIVED JULY 8, 1930 PUBLISHED NOVEMBER 5, 1930

Introduction

With the use of a sensitive differential calorimeter,[2] the integral heats of dilution of a number of strong electrolytes in water in the concentration range 10^{-1}–10^{-5} M have been measured in this Laboratory.[3] The thermodynamic usefulness of such quantities is illustrated, for example, in Latimer's treatment of the problem of aqueous ionic entropies.[4] For an exact comparison of the measurements with theoretical heats of dilution[5] calculated in accordance with the Gronwall, La Mer and Sandved[6] development of the fundamental theory of activity coefficients of Debye and Hückel,[7] an exact knowledge of dD/dT for the solvent is necessary. Unfortunately, the measurements at hand, even for water, show such discrepancies among the different series of results that such a comparison is at present somewhat uncertain.[8] The experimental results obtained with a number of 1–1 type salts may be summarized as follows: (a) the integral heat of dilution (V_c) is positive and is proportional to the square root of the concentration (expressed in moles of salt per liter of solution) from the most extreme dilution up to a concentration of about 0.01 M on the average; (b) the different salts have individual slopes in this concentration range $(V_c = A\sqrt{c})$, the individuality persisting down to the lowest measured concentration; (c) the values of the initial slopes A range from 280 to 430, which values correspond to 'a' values (apparent ionic diameters) of a reasonable order of magnitude, although, as mentioned, the uncertainty in the dD/dT value does not permit a more definite evaluation of these parameters.

It was thought of interest to extend these measurements to non-aqueous

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[1] Twenty-eighth Communication on Thermochemical Researches. A list of the previous papers in this series of thermochemical investigations by E. Lange and co-workers is given in *Z. physik. Chem.*, **148A**, 97 (1930).

[2] A detailed description of the calorimeter is given in Lange and Monheim, *ibid.*, **149A**, 51 (1930). A description of the calorimeter and a summary of the work on the heats of dilution of strong electrolytes will appear shortly in *Chemical Reviews.*

[3] Lange, Robinson, Monheim and Streeck, Z. *Elektrochem.*, 36, 772 (1930).

[4] Latimer and Buffington, THIS JOURNAL, 48, 2297 (1926).

[5] Lange and Meixner, *Physik.* Z., 30, 670 (1929).

[6] Gronwall, La Mer and Sandved, *ibid.*, 29, 358 (1928).

[7] Debye and Hückel, *ibid.*, 24, 185 (1923).

[8] Lange and Robinson, THIS JOURNAL, 52, 2811 (1930).

solvents where from all theoretical considerations the dielectric constant and dD/dT for the solvent in question should be the influencing factors in determining the values of the integral heats of dilution. The experimental difficulties are not much greater than in the case of aqueous solutions and it is intended to carry out such measurements in the near future. There is also the possibility of using as solvents aqueous solutions of non-conducting substances which alter the dielectric constant and dD/dT of water. In comparing the results obtained with aqueous solutions with the demands of the theory, the D and dD/dT values for pure water have been used; a justification for this usage has been shown by Debye and Pauling.[9] By the use of solvents such as those used in these measurements, it was hoped to bring further evidence to test whether the dielectric properties of the medium are the constants to be used for dilute salt solutions. In this paper are reported measurements of the integral heats of dilution of potassium chloride in a 15 weight per cent. aqueous solution of sucrose and a 5 weight per cent. aqueous solution of urea; for these two solvents there are dielectric constant and dD/dT measurements by Kockel.[10]

Experimental Results

Materials.—The potassium chloride was a de Haen guaranteed pure preparation which after drying was used without further purification. Previous experience with this salt had shown that traces of impurities did not influence the measured heats of dilution beyond the calorimetric error of ±2%. A fresh solution was prepared for each new concentration measurement.

Ordinary lump sugar was found to give results indistinguishable from a Kahlbaum preparation for thermochemical determinations and was, therefore, used for most of the sugar solution measurements.

The urea used was partly a pure preparation from Kahlbaum, and for a portion of the measurements a doubly purified preparation from de Haen. The two gave entirely concordant results.

Measurements.—For details of procedure in carrying out the measurements we refer the reader to previous publications.[11] The metal pipets containing the solution to be diluted had, respectively, volumes of 24.6 ± 0.1 cc. in the left half (l) of the calorimeter and 24.9 ± 0.1 cc. in the right half (r). The calorimeter halves were filled with 800 cc. (l) and 810 cc. (r) of solvent. After the solutions in both halves had been diluted, the pipets were pumped out and refilled with the same solution, so that so-called "second dilutions" could be carried out. As the concentrations in Tables I and II show, the end concentration after a "second dilution" was, with sufficient exactness, the same as the end concentration after a "first dilution" with a solution of double initial concentration, so that all measurements could be plotted on a common curve, practically without interpolation. Column 4 in the same tables shows the heat given to the opposite half—since all dilutions produced an evolution of heat—as compensation by electrical heating during the dilution, so that the temperature difference between the two calorimeter halves could be kept as small as possible. Column 6 gives the uncertainties in the

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[9] Debye and Pauling, THIS JOURNAL, 47, 2129 (1925).

[10] Kockel, *Ann. Physik*, 77, 430 (1926).

[11] In particular Lange and Monheim, *Z. physik. Chem.*, 149A, 51 (1930).

individual measurements due to the uncertainty in the extrapolation of the galvanometer readings before and after the dilution and does not take into account any systematic

TABLE I

HEATS OR DILUTION[a] OF POTASSIUM CHLORIDE IN 15% AQUEOUS SUCROSE SOLUTION AT 25°

Concentration mole/liter c_{initial}	c_{end}	Calorimeter Half	cal. compensation	cal. measured	cal. uncertainty	Heat of dilution cal./mole salt $Vc_{\text{in.}}\, c_{\text{end}}$	Mean
0.1	0.00308	(r)	0.1814	0.1838	0.0004	73.8	74.3 ± 0.5
.1	.00308	(1)	.1818	.1839	.0004	74.7	
.1	.00605	(r)	.3266	.3191	.0007	65.1	64.9 ± 0.2
.1	.00605	(1)	.2909	.3133	.0008	64.7	
.05	.00154	(r)	.0723	.0762	.0002	61.2	62.0 ± 0.6
.05	,00154	(1)	.0727	.0769	.0002	62.5	
.05	.00154	(r)	.0725	.0776	.0004	62.3	
.05	.00302	(r)	.1205	.1332	.0006	54.4	55.6 ± 0.8
5	0 0 0 2	(1)	1 2 1	1 3 5	0 0 0	56.1	
.05	.00302	(r)	.1208	.1388	.0010	56.2	
.025	.000770	(r)	.0241	.0283	.0003	45.4	47.0 ± 0.8
.025	.000770	(1)	.0242	.0289	.0002	47.0	
.025	.000770	(r)	.0241	.0290	.0003	46.6	
.025	.000770	(1)	.0242	.0296	.0003	48.2	
.025	.000770	(r)	.0241	.0297	.0005	47.7	
.025	.001515	(r)	.0481	.0519	.0005	42.3	42.7 ± 0.6
.025	.001515	(1)	.0483	.0531	.0006	43.9	
.025	.001515	(r)	.0482	.0508	.0008	41.5	
.025	.001515	(1)	.0484	.0521	.0005	43.1	
.025	.001515	(r)	.0482	.0525	.0010	42.8	
.0125	.000385	(r)	...	.0102	.0005	.	[illegible]
.0125	.000385	(1)	...	0 0 9	0 0 0	.	
.0125	.000385	(r)	...	,0109	.0006	35.1	
.0125	.000385	(1)	...	.0106	.0004	34.5	
.0125	.000754	(r)	...	.0191	.0010	31.3	31.7 ± 0.4
.0125	.000754	(1)	...	.0194	0 0 0	32.1	
.0125	.000754	(r)	...	.0189	.0010	30.9	
.0125	.000754	(1)	...	.0197	.0008	32.5	

[a] In the notation of Lewis and Randall, "Thermodynamics," pp. 88, $Vc_{\text{in.}}\, c_{\text{end}} = \overline{L}_{2\text{in.}} - \overline{L}_{2\text{end}} = \overline{H}_{2\text{in.}} - \overline{H}z.,$~and $V_c = \overline{H}z - \overline{\overline{H}}{}_2^0 = \overline{L}z$.

TABLE II

HEATS OF DILUTION OF POTASSIUM CHLORIDE IN 5% AQUEOUS UREA SOLUTION AT 25

Concentration mole/liter c_{initial}	c_{end}	Calorimeter Half	cal. compensation	cal. measured	cal. uncertainty	Heat of dilution cal./mole salt $Vc_{\text{in.}}\, c_{\text{end}}$	Mean
0.1	0.00308	(r)	0.1446	0.1432	0.0005	58.2	57.7 ± 0.4
.1	0 0 3 8	(1)	1	.1403	0003	57.1	
.1	.00308	(r)	.1445	.1438	.0003	57.7	
.1	,00605	(r)	.2530	.2435	-0009	50.4	50.0 ± 0.3
.1	0 6 0 5	(1)	2 5 2	1	0006	49.9	
.1	.00605	(r)	.2528	.2441	.0007	49.8	

TABLE II (*Concluded*)

Concentration mole/liter		Calorimeter	cal. compensation	cal. measured	cal. uncertainty	Heat of dilution cal./mole salt	
c_{initial}	c_{end}	Half				$V_{c_{\text{in.}}}$, c_{end}	Mean
0 05	0 00154	(r)	0.0483	0 0600	0.0004	48 2	49.0±0.8
.05	.00154	(l)	.0673	.0619	.0004	50.4	
.05	.00154	(r)	.0669	.0603	.0005	48.4	
.05	.00302	(r)	.0966	.1044	.0009	42 6	43 4±0 6
.05	.00302	(l)	.1076	.1072	.0008	44 3	
.05	.00302	(r)	.1072	.1062	.0010	43.4	
.025	.000770	(r)	.0268	.0243	.0003	39 5	37 9±0 8
.025	.000770	(l)	.0269	.0228	.0005	37.0	
.025	.000770	(r)	.0268	.0237	.0003	38 1	
.025	000770	(l)	.0269	.0228	.0003	37.0	
.025	.001515	(r)	0402	0424	.0006	35.0	34.3±0.4
.025	.001515	(l)	.0403	.0416	.0010	33.7	
.025	001515	(r)	.0402	0411	.0007	34.0	
.025	.001515	(l)	.0403	.0422	.0006	34.4	

TABLE III

INTEGRAL HEATS OF DILUTION (INTERPOLATED) AT 25°

Initial concentration in mole/liter		V_c in cal./mole of salt		Initial concentration in mole, liter		V_c in cal./mole of salt	
$\sqrt{c}$	c	KCl in 15% sucrose	KCl in 5% urea	$\sqrt{c}$	c	KCl in 15% sucrose	KCl in 5% urea
0.01	0.0001	4.0	3.4	0.19	0.0361	67.4	55.3
.03	.0009	11.7	9.9	.21	.0441	73.3	59.9
.05	.0025	19.3	16.6	.23	.0529	78.6	64.1
.07	.0049	27.2	23.1	.25	.0625	83.5	67.8
.09	.0081	34.8	29.2	.27	.0729	87.8	71.0
.11	.0121	41.6	35.1	.29	.0841	91.5	73.8
.13	.0169	48.7	40.7	.31	.0961	94.7	75.8
.15	.0225	55.4	45.6	.33	.1089	97.1	77.8
.17	.0289	61.5	50.4				

errors which may have been present. The latter may take the form of absorption heats, but from various considerations[12] we believe that such disturbing factors were not present. Moreover, the inner walls of the Dewar vessel were covered with a thin layer of pure vaseline. Controls in the form of blank runs repeatedly gave a zero galvanometer deflection when both pipets (filled with solvent or with the same solution that was contained in the calorimeter) were opened simultaneously. The sensitivity of the galvanometer was 0.0007 cal. per mm. of deflection or about 8×10^{-7}° per mm.; a greater sensitivity was not required for these measurements. The average reproducibility of the individual measurements was ±0.0004 cal., corresponding to about 4.5×10^{-7}°.

From the experimental data curves were plotted which showed, below 0.008 M, a proportionality with $\sqrt{c}$ within the limit of experimental error, and which were therefore extrapolated linearly to $c = 0$. The A values obtained by extrapolation are 386 ± 3% for the 15% sugar solution as solvent and 332 ± 3% for the 5% urea solution as solvent, as compared with 376 ± 3% for potassium chloride in pure water.[13] From the smooth curves the values for the integral heats of dilution given in Table III were ob-

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[12] Lange and Messner, Z. *Elektrochem.*, **33,** 439 (1927).

[13] Lange and Leighton, ibid., 34, 566 (1928).

tained. These values we believe to be exact to within ±2% plus an additive uncertainty of 0.5 cal. introduced by the extrapolation.

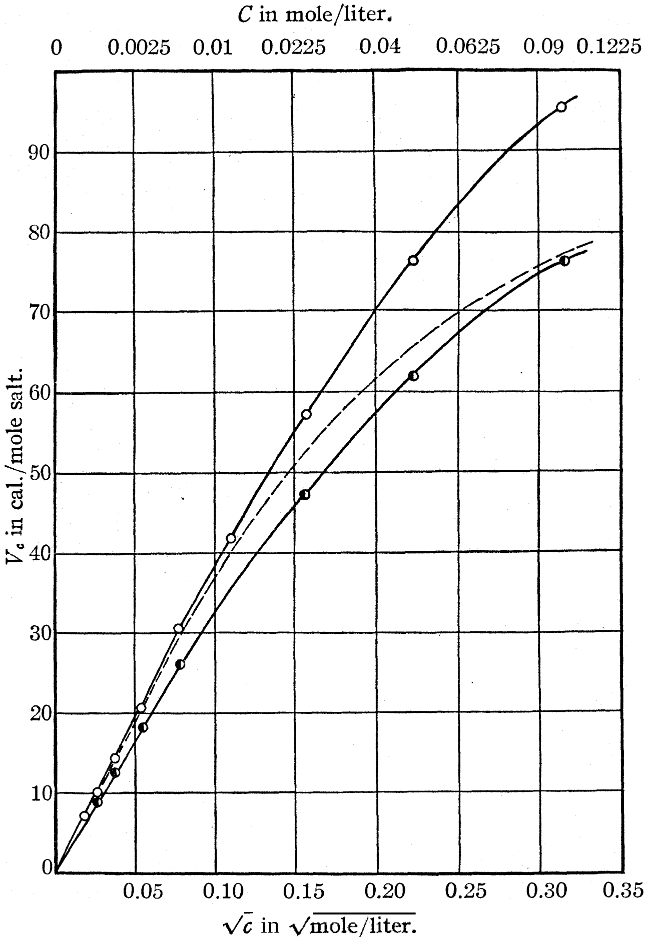

Fig. 1.—○, 15% sucrose; ◐, 5% urea; — — — —, water.

Discussion of Results

At first glance it is seen that the two measured dilution curves are entirely similar in their general nature to the previously obtained curves for potassium chloride and other 1–1 type salts in water; there is the same initial linearity with $\sqrt{c}$ and the initial slopes correspond well with the values mentioned above. However, the differences between the curves for the sugar and urea solutions as solvents and that for pure water, partly at low concentrations and partly at higher concentrations, are real and entirely outside of the experimental error. In the case of the sugar solution there is considerable evidence[14] to indicate that the sucrose molecules are hydrated, probably with approximately six water molecules, and the higher heats of dilution of the potassium chloride in this solvent might be explained as being caused by an increase in the potassium chloride concentration due to the removal of (6 × moles of sucrose) moles of water. A simple calculation shows that this explanation is inadequate, accounting at the most at a potassium chloride concentration of 0.1 M for but 10% of the observed difference. From the classical point of view another possible explanation is that the dielectric constant of this solution is, according to Kockel's measurements, about 5% lower than that of pure water and that if in these dilute solutions undissociated potassium chloride molecules are present, a larger number of such molecules might be expected in the solvent of lower dielectric power, accounting for the more positive values of V_c. But this explanation demands a positive dissociation heat for potassium chloride, which does not agree with the case for potassium chloride in pure water, where the effect of the hypothetical association at higher concentrations is to produce more negative heats of dilution.

There is also the possibility to consider of compound formation between the ions and the sugar or urea molecules, similar to the more or less stable binding of water molecules by the ions. In terms of the interionic theory this could be interpreted as a change—very likely an increase—in the '*a*' value for potassium chloride. A further discussion of this possibility does not seem possible in view of the lack of experimental facts.

Assuming that such effects are not present, an explanation for the experimental curves, not explainable by hydration of the sucrose molecules or an increased association of the potassium chloride, may be sought in a consideration of the dielectric properties of the solvents.

The relation of the initial slope ***A*** to the dielectric properties of the medium (limiting Debye–Hückel case) is shown by the equation

$$V_c = -1.66116 \times 10^7 \times 1/D \times 1/\sqrt{DT}(1 + T/D\ dD/dT)\sqrt{c} = A\sqrt{c}\ \text{cal./mole of salt}$$

Plotting Kockel's data, we have obtained the following values at 25°: for a 15% sugar solution D = 74.25 and dD/dT —0.38, for a 5% urea solution D = 82.8 and $dD/dT = -0.20$. The calculation of ***A*** gives +532 for the sugar solution and —228 for the urea solution as compared with +661 for pure water (again using Kockel's measurements for the sake of comparison). The great sensitivity of the factor $(1 + T/D \times dD/dT)$ to small changes or uncertainties in dD/dT makes impossible any certain decision in the case of the sugar solution, and water curves but, if Kockel's values for the urea solution are even only approximately correct, we should get a curve with a negative instead of a positive slope. The evident contradiction in this case could be avoided by using the D value for water, and

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[14] McBain **and** Kistler, *J. Phys. Chem.*, **33,** 1806 (1929).

not the D for the urea solution. On the other hand, there has been no doubt as yet in investigations of the activity coefficients of strong electrolytes in non-aqueous solvents that the D value of the particular solvent should be used.[15] Accordingly we should use the dielectric constants of these two solutions in question and in view of the unexplainable discrepancy in the case of the urea solution we might conclude that there is an error in the measured dD/dT value, although Kockel reported reproducible measurements in the temperature range 5–35'. The question seems to be interesting enough to warrant further accurate measurements of dD/dT for aqueous solutions of non-conducting substances, at least relative to the value for water, since the corresponding heat of dilution measurements can be made accurately and without great difficulty.

We thank the Notgemeinschaft der Deutschen Wissenschaft and the Kaiser Wilhelm Institut für Physik for their support in this work through the furnishing of necessary apparatus. One of us (A. L. R.) was on leave of absence from the University of Pittsburgh during the course of this work.

Summary

The integral heats of dilution of potassium chloride in a 15% sucrose solution and a 5% urea solution as solvents have been measured in the concentration range 10^{-1}–10^{-4} M at 25° with an exactness of ±2% plus an added uncertainty of 0.5 cal. introduced by the extrapolation to infinite dilution.

The curves are of the same general nature as those obtained for a number of 1–1 type salts (including potassium chloride) in water, but the deviations from the curve obtained for potassium chloride in pure water throughout the entire measured concentration range are outside of the limit of error.

It does not seem possible to explain these deviations in terms of concentration or association effects (if the formation of compounds between potassium chloride and sucrose or urea molecules is excluded). The differences are possibly due to the different dielectric properties of the solvents used, although uncertainties in the values of these constants make an exact comparison impossible.

MUNICH, GERMANY

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[15] *La Mer, Trans. Am. Electrochem. Soc.*, 51, 507 (1927).

[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

THE IGNITION OF CARBON MONOXIDE–OXYGEN MIXTURES: THE EFFECT OF IMPURITIES

BY A. KEITH BREWER AND W. EDWARDS DEMING

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Introduction

In a previous communication[1] it was shown that when a $2CO–O_2$ mixture was ignited by a condensed discharge a hyperbolic relationship existed between the gas pressure and the condenser voltage, i. e.,

$$V = k/P \qquad (1)$$

where V is the minimum voltage necessary for flame propagation and P is the pressure of the explosive mixture. The effects of various impurities on the ease of ignition were also discussed and an attempt was made to establish a mathematical relation between the amount of impurity and the energy of ignition.

In the present paper it is proposed to extend the hyperbolic relation between voltage and pressure to other explosive mixtures and to establish a more exact mathematical relation between the quantity of impurity present and the ignitibility of the gas.

Finch and Cowen[2] have shown that the ignition current in a $2H_2–O_2$ mixture is a hyperbolic function of the pressure over an appreciable pressure range. From this they drew the conclusion that "ignition is determined solely by the attainment in some portion of the gas traversed by the discharge of a certain definite concentration of suitable ions or electrically charged particles."

The study of the effect of impurities on the ignitibility of explosive mixtures has largely been confined to that of water vapor on the $2CO–O_2$ mixtures. This problem has been investigated by W. A. Bone and his co-workers[3] who have shown that as water vapor is progressively removed the ignitibility rapidly diminishes, the minimum spark energy for a mixture dried with calcium chloride being about thirty-fold that required to ignite the same mixture when saturated with water. They have also shown that gas dried for a year over phosphorus pentoxide is ignitible in a sufficiently powerful condensed discharge although the reaction does not go to completion.

Apparatus

The type of apparatus used in these researches was briefly described in the former article. It consisted of an explosion chamber of 56 cc. capacity which was connected

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[1] A. Keith Brewer, *Proc. Nat. Acad. Sci.*, 13, 689 (1927).

[2] Finch and Cowen, *Proc. Roy. Soc.* (London), 116A, 529 (1927).

[3] Bone and Weston, *ibid.*, 110, 615 (1926).

to separate gas trains, one for the admission of the moist or dried $2CO-O_2$ mixture, and the other for the admission of the various impurities tested.

Open-end mercury manometers were used to determine the gas pressures. A McLeod gage was unsuitable since most of the impurities tested were vapors. The glass walls of these manometers can be kept clean by admitting hydrogen to the system from time to time and then passing an electric discharge from the mercury to a suitably placed auxiliary electrode. The H_2^+ ions and atoms formed in the discharge readily reduce the oxides contaminating the walls.

A Hyvac pump capable of giving a pressure of less than 0.1 mm. was used for evacuation. The explosion chamber was flushed out before admitting fresh gas.

Connection to the explosion chamber was made through ground-glass stopcocks lubricated with high vacuum stopcock grease. No effect whatsoever could be attributed to the use of the grease. Its lower vapor pressure and its greater freedom from leaks render it far more satisfactory than the sirupy phosphoric acid often used in this type of work.

The ignition was brought about by a discharge from eleven 1-mf. condensers placed in parallel. The condensers could be charged to any desired voltage by a high voltage d. c, generator placed across a suitable potentiometer. The charging voltage was read with a 750 voltmeter, which could be used with a 10^5-ohm resistance in series when necessary.

The spark gap was made from two platinum balls about 2.0 mm. in diameter; one was fastened directly to a 60-mil tungsten lead while the other was fastened to a strip of flexible platinum spot welded to a tungsten lead on one end while the other end was connected to an iron weight enclosed in glass. The discharge 'was caused to pass by means of an electromagnet attracting the iron weight on the flexible platinum. The electrodes were removed from time to time and the balls re-rounded with an oxy-hydrogen flame; the shape of the electrodes had little effect, however, except when they were badly burned away.

The carbon monoxide was prepared by the action of formic acid on sulfuric acid. Electrolytic oxygen was used from which the hydrogen was removed with heated copper oxide and the water with sulfuric acid. The organic vapors were all dried and purified by the usual methods.

The $2CO-O_2$ mixture was dried by allowing the preliminary dried gases to stand over fresh sulfuric acid for about twenty-four hours, and then by passing the mixture through a deep tower filled with sulfuric acid and glass beads before entering the explosion chamber. Any sulfuric acid mist was removed with glass wool. Water was substituted for the acid when it was desired to have the mixture saturated with moisture.

Method of Procedure

In preparing the explosion chamber for a filling with a water-saturated $2CO-O_2$ mixture, no precautions were necessary after evacuation except to flush the chamber out with a small amount of gas before filling to the desired pressure. In the experiment, when the dry gas was used, the explosion chamber was baked out with a flame to remove all adhering moisture from the walls before starting the experiment. After the system was once thoroughly dried, further baking out was unnecessary during a single series of runs.

In testing for the effect of impurities it was found that *a* thorough mixing of the gases, as well as a more accurate pressure reading, could be obtained by admitting the impurities to the reaction chamber first. When necessary, the gases were agitated in the explosion chamber by swinging the flexible electrode with the electromagnet.

In determining the minimum ignition voltage, it was found necessary to obtain the approximate voltage first. This was done by starting at some low voltage and gradually raising the sparking voltage until the gas ignited. Since the sparking potential fluctuates statistically about a definite value for a given set of conditions, several tests had to be made at each voltage. It was found, in general, that if a gas mixture would ignite at a given voltage it would do so within three or four trials. After the approximate ignition voltage was found, the true voltage was obtained by starting the ignition tests just under the first value. Since some oxidation took place in the path of any spark the products of reaction formed before the ignition voltage was reached often caused these two values to differ by an appreciable quantity.

Results

Pure Explosive Mixtures.—The pressure ignition-voltage curve for an explosive mixture of ethyl ether and oxygen is illustrated in Fig. 1. The results obtained with explosive mixtures of oxygen with carbon disulfide, ethyl alcohol and carbon monoxide are similar. In most instances the points on a given curve checked within ±5 volts.

When the ignition voltage was plotted against the reciprocal of the pressure the points all fell closely on the straight lines illustrated in Fig. I. This indicates that a hyperbolic relationship exists between ignition voltage and pressure which may be expressed as $V = k/P$. It will be noted that while the values of k differ widely for different reactions, the lines all intersect the voltage axis some place between 15 and 20 volts.

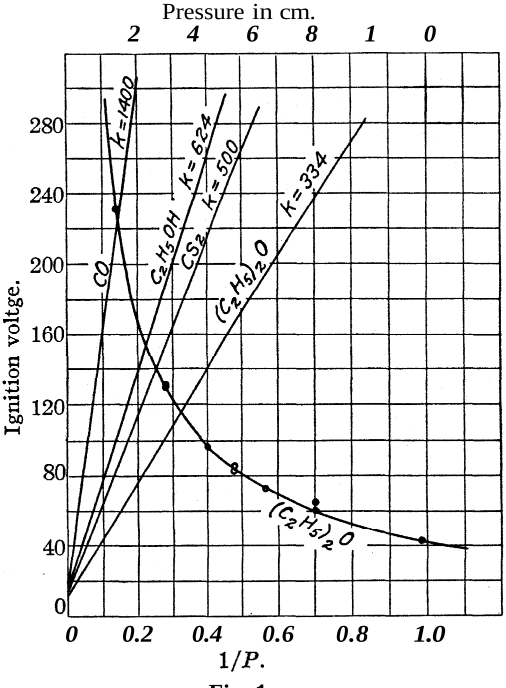

Fig. 1.

Effect of Impurities.—Impurities may be divided into two distinct classes with respect to their effect on the ignitibility of *a* $2CO–O_2$ mixture; namely, as positive and negative catalysts. The former are those that when added to the explosive mixture in almost any proportion lower the energy necessary for ignition, and the latter are those that raise the ignition energy.

In Fig. 2 is illustrated the effect of adding various amounts of impurities on the voltage necessary to explode a mixture containing 12 cm. $2CO + O_2$ and 2 cm. water vapor.

It will be noted that ether up to 3.0 mm. and ethyl alcohol up to 6.0 mm. partial pressure lower the ignition energy, and thus behave as positive catalysts. Above these pressures the vapors of both behave as powerful negative catalysts.

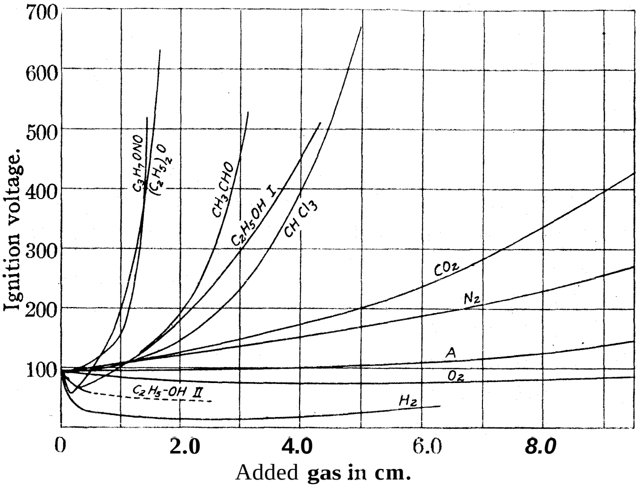

Fig. 2.

The ethyl alcohol curve is divided into two sections: Part I represents the addition of alcohol vapor alone, while Part II represents the effect produced when sufficient oxygen to burn the alcohol is also added. The effect of ether with additional oxygen is the same. Hydrogen also behaves, in this respect, like alcohol and ether, but the effect is not so pronounced. The reason is probably that the hydrogen burns even without additional oxygen because it ignites more readily than the carbon monoxide and requires much less oxygen per volume than alcohol or ether. Thus it will be seen that whether these vapors are to be considered as positive or negative catalysts depends entirely on whether or not they burn in the explosion; if they burn, they are positive catalysts, while if oxygen is insufficient for their combustion, they are negative catalysts.

The data in Fig. 1 show that gases differ widely in their negative catalytic properties. To illustrate, the amount of impurities in centimeters of mercury that must be added to a given explosive mixture to raise the ignition voltage from 95 volts to 150 volts is as follows.

Impurity	Cm of Hg	Impurity	Cm. of Hg
A	9.75	C_2H_5OH	1.7
N_2	4.0	CH_3CHO	1.6
CO_2	3.0	C_3H_7ONO	0.95
$CHCl_3$	2.2	$(C_2H_5)_2O$	.80

It will be seen from the foregoing that the ability of an impurity to inhibit ignition is a function of the complexity of the molecule; indeed it is almost directly proportional to the number of atoms in the molecule. An exact mathematical relationship between the number of atoms and the ignition voltage is difficult to establish, since many of the impurities such as hydrogen and alcohol behave both as positive and negative catalysts, depending on the amount present.

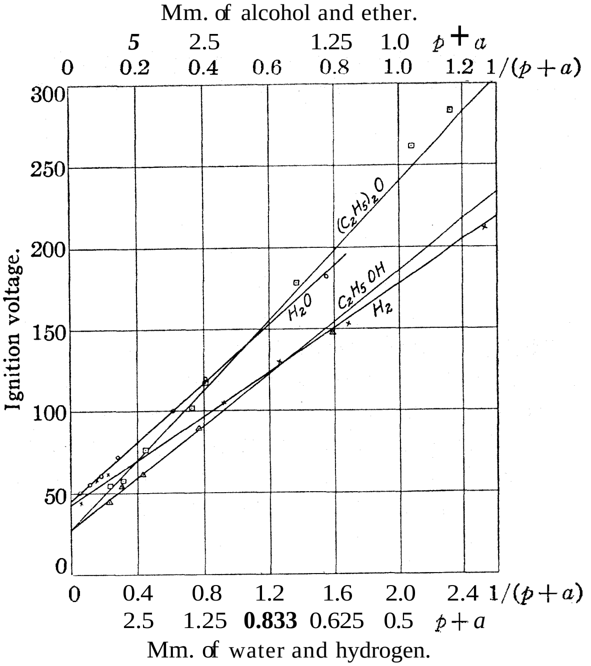

Fig. 3.

Quantitative Effects of Four Positive Catalysts.--The effect of adding explosive mixtures of oxygen with hydrogen, water, alcohol and ether vapors as impurities to the dry $2CO-O_2$ explosive mixture at 14 cm. pressure is exhibited in Fig. 3. The abscissas are $1/(p + a)$, where p mm. is the observed pressure of gas added, and a is a constant that differs from one gas to another. The ordinates are the voltages necessary to ignite the mixture when the p mm. of gas have been added; p and V seem to satisfy the relation

$$V = \frac{c}{p + a} + b \qquad (2)$$

This is the equation of the lines drawn in the figure. The values of a, b, c are tabulated below.

Gas	a (mm)	b (volts)	c (mm. volts)
Water	-0.35	45.4	90.2
Hydrogen	.10	42.7	67.6
Alcohol	.67	27.3	158.9
Ether	.46	27.4	213.8

These values were worked out by least squares, throwing all the errors of observation on to p, and giving the higher values of p several times as much weight as the lower values.

It is interesting to observe that the points satisfy this relation as closely as they do, that the V intercepts for hydrogen and water are nearly equal, and that those for alcohol and ether are equal. These curves, if extended, would not be straight lines throughout their entire course; at their upper ends they must all become asymptotic to the ignition voltage for the pure $2CO-O_2$ mixture at 14-cm. pressure. At the lower ends beyond the last experimental points, their shapes cannot be predicted with certainty, but the curve for water will turn up and become asymptotic to the V axis. Over the range of these experiments the data are well represented by the relation (2).

An explanation of the constant a that enters the above relation can be found from the following reasoning. The impurity was always admitted to the explosion chamber and its pressure p read before the explosive mixture was turned in. The pressure of the impurity was in most cases comparatively small—from 0.2 mm. to 20 mm.—and if a few tenths of a millimeter of the gas condensed on the walls after it was read, or if some that had already condensed before its pressure was read was displaced by the carbon monoxide or oxygen, then the pressure of the impurity actually in the gas phase at the moment of explosion would differ from the value recorded for #. It seems plausible to consider that a represents the average discrepancy between p and the actual pressure $p + a$ of the impurity at the moment of explosion. $1/(p+a)$ could then be considered the specific volume (in arbitrary units); and since the curves are straight lines it appears that the change in ignition voltage is proportional to the change in the specific volume of the impurity present at the moment of ignition.

Discussion

A consideration of the ignition process is helpful to an understanding of the mechanism. A critical voltage exists for each explosive mixture, and propagation never takes place at lower voltages. Chemical action does take place, however, directly in the path of the spark at a voltage far below that necessary for propagation. The amount of gas burned in the non-propagating sparks was measured by the change in pressure following the spark; when low voltages were used it was found necessary to measure the pressure after several sparks had been sent through the gas. In gases with a low ignition voltage, the amount that can be burned in a non-propagating discharge is small, but for a dried $2CO-O_2$ mixture, which has a high ignition voltage, a discharge wherein slightly over one cubic centimeter of gas, at the pressures used, is burned in the spark can be sent through the gas without propagation. For the moist mixture the gas that could be burned in a non-propagating spark was of the order of 1 to 5 cubic millimeters; the size of the ball of gas burning in the path of the spark increases with the decrease in percentage of moisture. It appears, therefore, that a certain amount of the mixture must be burned in the spark before the combustion will go to completion; the higher the ignition voltage the more must be burned in the spark.

In the case of the added impurities, it will be seen in Fig. 2 that both alcohol and ether in themselves are strong negative catalysts in the oxidation of carbon monoxide, while in Fig. 3 both of these vapors, in the presence of sufficient oxygen for their combustion, appear as powerful positive catalysts. From this it appears that ether and alcohol molecules, as such, are negative catalysts and that the burned product is the positive catalyst. Since carbon dioxide, as will be seen in Fig. 2, shows only negative catalytic properties, it follows that the positive action of both alcohol and ether as well as hydrogen is largely due to their ability to furnish water to the reaction. No doubt the heat liberated in this oxidation is also a contributing factor, but is of minor importance compared to the formation of water.

A comparison of the slopes of the lines in Fig. 3 shows that per total water molecules formed there is a decreasing efficiency per molecule in the order water, hydrogen, alcohol and ether, probably because the effective water concentration is materially less than the total number formed in the explosion, since the rate of burning of carbon monoxide is appreciable compared with that of the hydrogen, alcohol or ether. In the two latter cases the apparent efficiency of the water is also impaired by the presence of carbon dioxide.

These observations confirm the relation that has been shown to exist between ignition voltage and pressure. The equation $V = k/P$ shows that the ignition voltage is inversely proportional to the pressure and hence to the number of molecules in the path of the spark. Thus for propagation it appears that a definite number of molecules must be burned in the path of the spark, the exact number being specific for each reaction. While the number of molecules that must he burned for propagation cannot be told, the relative number for different mixtures may be obtained from the values of k; since the slopes of the lines of V vs. $1/P$ are 1400 and 334 for carbon monoxide and ether, respectively, we can say that the number of molecules that must be burned for propagation in the two mixtures are in the ratio 1400:334. This statement assumes that density is proportional to pressure, and that the lines all have the same intercept on the V axis, both of which are not strictly true but introduce only small corrections. k can therefore be used as a measure of the ease of ignition in various explosive mixtures and may be termed the *ignitibility constant.*

In a condensed discharge, such as was used in this work, the quantity of electricity passing across the spark is proportional to the voltage, since $Q = CV$, where Q is expressed in coulombs, C is the condenser capacity, which was kept constant, and V is the voltage. The word *quantity,* therefore, can be substituted in the place of *voltage,* in these discussions.

In this connection it is of interst to recall that in a former article[1] it was shown that when the capacity was varied a 600% increase in C resulted in only an 18% decrease in Q. From this it will be seen that the ignition is actually established by the quantity of electricity flowing and is at most only slightly related to the voltage. The slight increase in Q with increased V and decreased C is probably because the ionizing efficiency of an electron is slightly less than proportional to the voltage. From these considerations it seems very probable, as was pointed out by Finch and Cowen,[2] that ignition results from the attainment of a definite ion density as determined by Q at some point in the gas.

The fact that the lines for the various gases listed in Fig. 1 intersect the voltage axis at a point that is very close to the ionization potential for the gases used indicates that ionization is necessary for ignition. In this respect the results are very similar to those obtained in the glow discharge, for the oxidation of hydrogen[4] and the oxidation of carbon monoxide,[5] wherein it was possible to trace the oxidation from a simple ionic reaction through chain reactions to the ignition point.

Laws of Ignition.—These observations, when interpreted in the light of the hyperbolic relation between pressure and ignition voltage, may be summed up in the following rules for ignition.

Equation 1 may be interpreted as: *(I) the voltage necessary to ignite a given explosive mixture is inversely proportional to the number of molecules in the path of the spark.* Similarly, Equation 2 may be interpreted: *(II) the ability of a positive catalyst to lower the voltage necessary to ignite a given explosive mixture is, over a wide range, proportional to the number of its molecules in the path of the discharge.* The data tabulated in Fig. 1 may be interpreted as: *(III) the ability of a negative catalyst to raise the ignition voltage is a direct function of the complexity of its molecule.*

Summary

The hyperbolic relation $VP = k$ between ignition voltage and pressure of the mixture, noted by Brewer in 1927, working with a $2CO-O_2$ mixture,

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[4] Brewer and Westhaver, *J. Phys. Chem.*, 34, **2343** (1930).

[5] Brewer and Kueck, *ibid.* (in press).

is shown to hold also for explosive mixtures of oxygen with ethyl alcohol, ether and carbon disulfide. Arguments are advanced to prove that this is a general law of ignition. k is different for each mixture.

Impurities in the explosive mixture are divided into two classes, positive and negative catalysts; the former lower the ignition voltage and the latter raise it. Vapors that burn to form water as one product of combustion will be positive catalysts when present in a small amount and negative catalysts when present in a greater amount. The positive action of a catalyst probably comes from the water formed in its combustion, which precedes the ignition of the main mixture. All impurities that form water seem to act as positive catalysts when present in *any* amount provided there is sufficient extra oxygen to burn the catalyst.

A quantitative relation, also hyperbolic, is worked out for impurities that act as positive catalysts. It is

$$(V - b)(p + a) = c$$

$p + a$ is the pressure of the explosive mixture added as impurity, V the ignition voltage, and b and c are constants for each catalyst.

The two hyperbolic relations explained can be restated thus: *(I) the voltage necessary to ignite a given explosive mixture is inversely proportional to the number of molecules in the path of the spark. (II) the ability of a positive catalyst to lower the voltage necessary to ignite a given explosive mixture is, over a wide range, proportional to the number of its molecules in the path of the discharge.*

A study of curves for several catalysts shows that, *(III), the ability of a negative catalyst to raise the ignition voltage is a direct function of the complexity of its molecule.*

WASHINGTON, D. C.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 5]

THE ANHYDROUS LOWER BROMIDES OF TITANIUM

BY RALPH C. YOUNG WITH WALTER C. SCHUMB

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Considerable work has been done on the anhydrous trichloride and dichloride of titanium, and the di-iodide and trifluoride have been prepared, but we have been unable to find any data concerning the anhydrous lower bromides. The present work had for its purpose the preparation of these latter compounds and a study of some of their properties.

Three methods of preparation were considered and tried: (1) reduction of the tetrabromide by hydrogen; (2) the action of hydrogen bromide on titanium; (3) reduction of the tetrabromide by metals with and without a solvent.

For the preparation of titanium tetrabromide, dry carbon dioxide was allowed to pass through an intimate mixture of pure titanium dioxide (1 mole) and charcoal (2 moles) which was heated in a combustion furnace. After the water vapor was expelled, the carbon dioxide was directed through liquid bromine and the temperature of the furnace was raised until the pyrex tube showed signs of softening. The titanium tetrabromide was collected in a pyrex flask connected to the reaction tube. It was later freed from bromine by being kept in a liquid condition while carbon dioxide was allowed to bubble through it. It was distilled in an atmosphere of carbon dioxide and collected in tubes which were then sealed The portion distilling at 230° was used. Titanium tetrabromide prepared by the action of hydrogen bromide on titanium was also used in some of the experiments.

In applying method (1) above mentioned, on account of the reversibility of the reaction between titanium tetrabromide and hydrogen, it seemed advisable to employ the hot–cold tube principle which was used in the preparation of the trichloride by Georges and Stahler.[1] Hydrogen, dry and freed from oxygen by passage over hot platinized asbestos, was allowed to bubble through liquid titanium tetrabromide in a 50-cc. flask, (A Fig. 1), sealed directly to a 30-mm. pprex tube, 66 cm. long, B, through the center of which passed an 8-mm. tube, C. Cold water was conducted to the end of tube C by a 4-mm, tube, D. By this means a temperature gradient in the outer tube of about 750 to 22° was obtained. A hinged type electric furnace was used for heating, the temperature of which was controlled by a rheostat and measured by means of a pyrometer.

Preparation of Anhydrous Titanium **Tribromide.**—The apparatus was first swept out with hydrogen which entered through a tube sealed to the neck of the flask. After the reaction tube had been heated to redness, the gas was directed through the titanium tetrabromide, which was heated with a burner to such a temperature that about 15 g. per hour was vaporized and passed into the large tube. It was found necessary to employ a rapid stream of hydrogen (about 200 cc. per minute) to insure appreciable yields of product. A dark deposit could be noticed almost immediately at the end of the cold tube. This grew in length and thickness. Some of the reduced product was carried along with the unchanged titanium tetrabromide and hydrogen through tube E into a flask, F, by means of which the unchanged titanium bromide could be recovered.

The deposit on tube C soon assumed a crystalline character. Lustrous blue-black needles extended from the portion adhering to the cold tube to within a few mm. of the walls of the outer tube. Interspersed among the needles were small hexagonal plates. This formation of needles and plates was allowed to continue for about two hours or until it had extended for a distance of about 10 cm. along tube C. The passage of the hydrogen

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[1] Georges and Stähler, *Ber.*, 42, 3200 (1909).

through the titanium tetrabromide was discontinued and the gas allowed to go directly into the reaction tube. The burner and the furnace were shut off and the reaction tube cooled to 250° and then the water flow was discontinued. Any titanium tetrabromide which had condensed on the cooling tube now volatilized. The furnace was next allowed to cool down to room temperature. All the titanium tetrabromide was driven by means of a free flame into the flask, F. Then a current of dry carbon dioxide was substituted for the hydrogen and after the hydrogen was displaced, the tube leading into the flask F was sealed at K. The empty cooling tube was next partly withdrawn through the cork stopper which held it in the large reaction tube. During this process a lively stream of carbon dioxide prevented air from entering through the cork. The black product for the most part fell to the bottom of tube B and by means of tipping and shaking could be brought into tube E without any appreciable hydrolysis taking place. After the flow of carbon dioxide had been stopped, the tube E was sealed at G and the product thus obtained in an atmosphere of carbon dioxide.

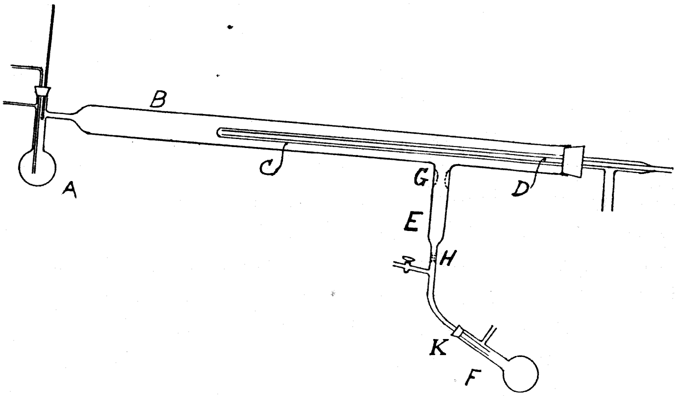

Fig. 1.—Apparatus for the preparation of titanium tribromide.

The tube with contents (carbon dioxide and the bromide of titanium) was weighed, opened and the product immediately dissolved in cold water. The familiar violet solution of trivalent titanium was obtained. There was a slight residue of titanium dioxide which amounted to 0.0035 g. in about 0.50 g. of the product. The titanium was removed from solution by precipitation with ammonium hydroxide as the hydrated oxide, which was afterward ignited and weighed as titanium dioxide. The bromine was determined as silver bromide.

ANALYSES

	I	II	Calcd. for $TiBr_3$
Ti, %	16.6	16.6	16.7
Br, %	83.0	82.9	83.3

The solution had the usual reducing properties of trivalent titanium. Ammonia produced a bluish-black precipitate which evolved hydrogen and gradually turned white.

During the course of one hour about one gram of the tribromide was produced and the tetrabromide which passed through the tube unchanged was recovered practically quantitatively.

An examination of the plates and needles was kindly made by Professor M. J. Buerger of the Geology Department of this Institute, who reported as follows. "The plates were hexagonal. The needles were studied with a petrographic microscope, carbon tetrachloride being used as the immersion liquid. The following characteristics were observed. With the light vibrating parallel to the length they were opaque, while they appeared blue with the light vibrating normal to the length. The interference colors can be described as anomalous. The needles possessed parallel extinction which denoted them to be hexagonal, tetragonal or orthorhombic. The formation of two kinds of crystals by a single substance in a reaction where a large temperature gradient is present is described by Tutton[2] in the case of antimony trioxide." The plates dissolved a little more slowly than the needles but gave the same violet solution. They seemed more compact and denser than the needles. Slight hydrolysis and oxidation brings about a somewhat violet appearance which deepens to red if allowed to continue.

Preparation of Anhydrous Titanium Dibromide.—The sealed tube containing a sample of the tribromide was evacuated with a high vacuum pump and heated in an electric furnace, the small end being immersed in ice water or in a mixture of alcohol and solid carbon dioxide. In decomposing the titanium tribromide, according to the equation $2TiBr_3 \qquad TiBr_2 + TiBr_4$, a temperature not greatly exceeding 400° was used in order to prevent as far as possible the decomposition of the dibromide; a 0.5-g. sample required eighteen hours for complete reaction. The proportions of dibromide and tetrabromide obtained from a known weight of the tribromide corresponded fairly closely to the requirements of the above equation. The titanium dibromide proved to be a deep black powder.

The end of the tube containing the volatilized titanium tetrabromide was sealed at H, the tube containing the dibromide was opened in an atmosphere of carbon dioxide and the contents dissolved in cold water saturated with carbon dioxide. A small residue remained undissolved which amounted to 0.0060 g. for 0.2100 g. of the product. Analysis gave the following results.

ANALYSES

	I	II	Calcd. for $TiBr_3$
Ti, %	77.5	77.3	76.8
Br, %	22.3	22.8	23.1

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[2] Tutton, "Crystallography and Practical Crystal Structure," p. 1256.

The black powder was very reactive, with strong reducing properties. It caught fire when exposed to moist air and dissolved in water with the evolution of hydrogen. In a mixture of ice and water saturated with carbon dioxide the reaction was much slower but nevertheless noticeable. On heating, titanium dibromide was found to decompose into titanium and titanium tetrabromide. This reaction takes place very slowly at 500°, but at 650° at such a rate that 0.2 g. decomposed in six hours. There was no evidence of hydrogen or hydrogen bromide being formed by the decomposition, which rules out the possibility of hydrogen being a part of the compound; nor was there any appearance of free bromine.

The following equations indicate two possible ways in which titanium tribromide could be formed from the tetrabromide:

$$2TiBr_4 + H_2 \rightleftharpoons 2TiBr_3 + 2HBr \qquad (1)$$

$$TiBr_4 + TiBr_2 \rightleftharpoons 2TiBr_3 \qquad (2)$$

The surface of the reaction tube in the hot zone is considerably attacked and black metallic titanium is first formed thereon. This then appears to react with the glass. It is reasonable to suppose that titanium dibromide is formed by reduction in a somewhat cooler zone and it was proved by a separate test that titanium tribromide can be formed with the furnace at 400°. In other experiments, a thermocouple enclosed in a pyrex tube in the reaction zone midway between the cooling tube and the inner surface of the large tube, which was heated to 750°, registered 400°. No reduction product was obtained on the side toward the hot surface of the large tube, while the product did form between the tube containing the thermocouple and the inner cold tube. The formation therefore took place below 400°.

A study was made of Reaction 2. In the same apparatus used for the preparation of titanium tribromide, titanium dibromide was formed in an atmosphere of hydrogen according to the equation $2TiBr_3 \qquad TiBr_4 + TiBr_2$, at 450°, no water having been allowed to circulate in the cooling tube. The needles and plates ($TiBr_3$) changed to a very black powder. Titanium tetrabromide was then passed with hydrogen through the furnace and the temperature gradually raised from room temperature. At 280° there developed the distinctive bluish-black appearance of the tribromide and at 380° all appeared to be changed over. The product dissolved in water to form a solution which possessed the properties of trivalent titanium.

Action of Hydrogen Bromide on the Lower Bromides of Titanium and Titanium Metal.—Titanium tribromide was made as described previously and hydrogen bromide, prepared as usual from hydrogen and bromine with the aid of a platinized asbestos catalyst, and carefully freed from bromine by ferrous bromide and from water by calcium bromide, was passed through the reaction tube containing the solid. The furnace temperature was gradually raised; at 250° reaction took place slowly with the formation of titanium tetrabromide and hydrogen and above 350° became very rapid.

Likewise, titanium dibromide was produced in the large pyrex reaction tube in the manner described above, hydrogen bromide was passed over it, and the temperature of the furnace gradually raised. The black titanium dibromide began to assume the brilliant blue-black color of the titanium tribromide at 160° and some titanium tetrabromide was also produced. The non-volatile product was dissolved in water and proved to be titanium tribromide.

Titanium metal was found to react with hydrogen bromide at 300° and very slowly slightly below this temperature. Experiments were conducted at 450° and at 300° to see in which case more of the non-volatile bromides were produced. At 450° the proportion of non-volatile product to volatile titanium tetrabromide, calculated in moles, was 1 to 20, while at 300° the proportion was 1 to 2 and only in the latter case was there evidence of the presence of the dibromide. Consequently the formation of incompletely halogenated products is favored by low temperature, a result which is similar to that noted in the action of hydrogen bromide on silicon.[3]

Finally, the reduction of titanium tetrabromide by means of metals, namely, titanium, mercury and silver, was studied. Titanium tetrabromide was heated with titanium in a sealed tube at 300° for four hours. Black needles of titanium tribromide, of the same general appearance as already described, were formed. Mercury was also found to reduce titanium tetrabromide when the two substances were heated in a sealed tube at 300°. If a sealed tube containing a benzene solution of titanium tetrabromide and mercury is rotated, the reduction to titanium tribromide and mercurous bromide is practically quantitative,* both products being insoluble in benzene. Attempts to separate the two by sublimation were not successful. Water dissolved the titanium compound and the solution gave the usual tests for trivalent titanium. Silver was found to react in a manner similar to mercury.

Summary

Anhydrous titanium tribromide was prepared in a mixture of two crystalline forms by reduction of the tetrabromide with hydrogen by the use of the hot-cold tube principle. In the study of its properties, it was found to decompose at 400° into titanium tetrabromide and titanium dibromide. The reverse reaction was also carried out by the passage of vapors of the tetrabromide over heated titanium dibromide. Titanium dibromide de-

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[3] Schumb and Young, THIS JOURNAL, 52, 1464 (1930).

[4] The titanium tribromide formed from 4 g. of titanium tetrabromide by reduction with 10 g. of mercury in 20 cc. of benzene reduced 26.5 cc. of 0.4 N ferric alum solution. This is equivalent to a yield of tribromide of about 97%.

composes into titanium metal and titanium tetrabromide, very slowly at 500° but rapidly at 650°.

Both the di- and tribromide react with hydrogen bromide to produce the tetrabromide. Titanium metal reacts with hydrogen bromide to produce a greater proportion of non-volatile bromides ($TiBr_2$ and $TiBr_3$) to the tetrabromide at 300° than at 450°.

At 300° titanium metal suspended in titanium tetrabromide brings about partial reduction to the tribromide. Silver and mercury reduce titanium tetrabromide, dissolved in benzene, to titanium tribromide; in the case of the latter metal the reduction is practically quantitative.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 247]

THE THERMODYNAMIC TREATMENT OF CHEMICAL EQUILIBRIA IN SYSTEMS COMPOSED OF REAL GASES. III. MASS ACTION EFFECTS. THE OPTIMUM HYDROGEN: NITROGEN RATIO FOR AMMONIA FORMATION IN THE HABER EQUILIBRIUM

BY LOUIS J. GILLESPIE AND JAMES A. BEATTIE

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Although the mass action law has often been applied to experimental studies of gaseous equilibrium, there is little or no direct evidence of its inadequacy for gases. This is doubtless due to the fact that most studies have been made at low pressures. and sometimes also at high temperatures, conditions which favor the applicability of the ideal gas laws to real gases.

A recent exception has been furnished by the data on the Haber equilibrium obtained by Larson and Dodge and by Larson.[1] Here it has been found that K_p, the mass action function in terms of ideal gas partial pressures, is not constant at constant temperature, as required by the theory of ideal gases, but increases definitely with the pressure. As already pointed out[2] we must therefore believe that K_p will vary if the concentrations are varied at constant temperature and pressure—in other words, that K_p is not strictly constant with respect to any change of condition whatever.

The contributions of previous investigators to the theory have been discussed at length in Part I of the present series[3] of three papers. Here we shall repeat only the previous results of present interest.

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[1] Larson and Dodge, THIS JOURNAL, 45, 2918 (1923); Larson, *ibid.*, 46,367 (1924).

[2] Gillespie, *ibid.*, 47, 305 (1925).

[3] Gillespie and Beattie, Phys. *Rev.*, 36, 743 (1930); Part II, *Phys. Rev.*, 36, 1008 (1930). In this part the heat of reaction was calculated at various temperatures and pressures, and the entropy and energy constants of ammonia were found.

In brief, a general mass action equation has been derived[4] by assuming that certain properties[4,5] of ideal gases hold also for real gases at very low pressures. By assuming further that the equation of state of a gas mixture may be obtained by means of a "linear combination of constants" and that the Beattie–Bridgeman equation of state[6] is to be used for the separate gases a mass action equation has been derived[7] in which all the integrations have been carried out, in terms of the volume of the mixture.

Subject to the same assumptions and to some simplifying assumptions, which should be valid at pressures not too high, the following approximate mass action equation has been derived[8]

$$\ln K_p = \ln K_p^* - \{\Sigma\nu_i[B_{0i} - A_{0i}/RT - C_i/T^3] + \Sigma\nu_i[(A_{0i}^{1/2} - \Sigma x_i A_{0i}^{1/2})^2/RT]\}p/RT \quad (1)$$

K_p^* is the limiting value of K_p when the gaseous mixture is maintained in equilibrium and its pressure reduced to zero. It is determined by the temperature alone for a given chemical equation.

An approximate equation similar to Equation 1, but without the constant c, has been obtained by Keyes[9a] from the kinetic considerations leading to the Keyes equation of state.[9b]

The chemical equation for the Haber equilibrium is

$$1/2N_2 + 3/2H_2 = NH_3 \quad (2)$$

From the definition of K_p we have

$$\log K_p = \log x - 1/2 \log x_N - 3/2 \log x_H - \log p \quad (3)$$

where x, x_N and x_H are the mole fractions of ammonia, nitrogen and hydrogen, respectively, in the equilibrium mixture, and p is its pressure.

Equation 1 gives us for the Haber equilibrium, after substituting numerical values[3] for the equation of state constants A_{0i}, B_{0i} and C_i

$$\log (K_p/K_p^*) = p[0.1191849/T + 25122730/T^4 + 38.76816\Sigma(x_i A_{0i}^{1/2})/T^2 + 64.49429(\Sigma x_i A_{0i}^{1/2})^2/T^2] \quad (4)$$

where the values of $A_{0i}^{1/2}$ for ammonia, nitrogen, hydrogen and argon are 1.546932, 1.159526, 0.4444097 and 1.136090 liter-(atmosphere)$^{1/2}$ per mole, respectively, and log refers to the base 10.

In Part I of the present series, Equation 4 was applied to the existing data of Haber,[10] of Larson and Dodge, and of Larson, and was found to represent the effect of pressure on the yield of ammonia within the experimental error at all temperatures.

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[4] Gillespie, THIS JOURNAL, 48, 28 (1926).

[5] Beattie, Phys. Rev., 36, 132 (1930).

[6] Beattie and Bridgeman, Proc. Am. Acad. Arts Sci., 63, 229 (1928); THIS JOURNAL, 50, 3133 (1928).

[7] Beattie, Phys. Rev., 31, 680 (1928); ibid., 32, 691 (1928).

[8] Gillespie, ibid., 34, 1605 (1929).

[9] (a) Keyes, THIS JOURNAL, 49, 1393 (1927); (b) Am. Soc. Refrig. Eng. J., 1, 9 (1914); Proc. Nat. Acad. Sci., 3, 323 (1917).

[10] Haber. Z. Elektrochem., 21, 89 (1915).

The temperature variation was expressed by the equation

$$\log K_p^* = -2.681122 \log T - 5.519265 \cdot 10^{-5} T + 1.848863 \cdot 10^{-7} T^2 + 2001\,6/T + 2.6899 \qquad (5)$$

of which the last two constants, and these only, were arbitrary and chosen to fit the whole body of data.

Theory

Equation 5 rests on the assumptions that the specific heats of the gases at extremely low pressures may be expressed over the necessary temperature interval a .functions of the temperature in series, and that the temperature variation of K_p is the same for real gases at extremely low pressures as for ideal gases.[11] There would be no point here in questioning the validity of these assumptions. The use to which we put Equations 4 and 5 in this paper depends, however, on the validity of Equation 1 or 4.

We believe that we are in a very good position to calculate the effects of varying composition in the Haber equilibrium by the use of the numerical equation 4 in connection with Equation 5, which serves to eliminate log K_p^* from Equation 4, for the following reasons: (1) the general assumptions underlying the mass action equations discussed above are supported abundantly by experimental evidence other than that relating to the Haber equilibrium, as has been discussed in Part I. (2) The agreement of the approximate equation (1) or (4) with the Haber equilibrium data indicates that the simplifying assumptions which have been used to obtain them are not too severe. (3) The composition terms in $\Sigma(x_i A_{0i}^{1/2})$ occurring in Equation 1 or 4 must be supposed approximately correct, since a mass action equation, which may be considered to be based on the Lewis and Randall rule[12] of fugacities, and which differs from Equation 1 principally by the omission of these composition terms, has been applied to the Haber equilibrium data and found to fail badly at 300 atmospheres to represent the pressure variation of K_p, though the representation at lower pressures was good.[4]

A mass action question of unique interest is the following: At what mole ratio, hydrogen:nitrogen, will there be at given temperature and pressure the largest mole fraction of ammonia in the equilibrium mixture?

When the function K_p is constant at constant temperature and pressure, as is the case not only for ideal gases but also for the case that the Lewis and Randall rule is exact,[4] the optimum ratio is exactly three (provided neither reactant is contaminated with an inert gas), as may readily be shown mathematically by equating to zero the derivative of log K_p with respect to the ratio H_2:N_2. But according to Equation 1 or 4, or indeed according

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[11] For a very simple choice of necessary assumptions for the discussion of thermodynamic equilibrium in real gases, see Beattie, Ref. 5.

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

to any equations which are not based on the ideal gas laws and which differ from the Lewis and Randall rule,[4] K_p varies with composition at constant temperature and pressure, and naturally a value different from three will be expected for the optimum ratio, as already suggested.[13]

By examination of the derivative of the mole fraction of ammonia at equilibrium, below always denoted by x, with respect to r_e, the equilibrium value of the ratio H_2:N_2. the following equation is found for the optimum value of r_e when no argon is present in the reactant gases.

$$r_e = 3 - \frac{2}{M}(A_{0N}^{1/2} - A_{0H}^{1/2})\frac{r_e}{(1 + r_e)}(1 - x)\left[38.768 + 128.99\Sigma(x_iA_{0i}^{1/2})\right]\frac{p}{T^2} \qquad (6)$$

Here A_{0N} and A_{0H} are the cohesive pressure A_0 constants in the Beattie–Bridgeman equation of state for nitrogen and hydrogen, respectively. The summation $\Sigma(x_iA_{0i}^{1/2})$ is obtained by adding the terms $x_1A_{01}^{1/2} + x_2A_{02}^{1/2} + \ldots$, etc., taking the square roots of the cohesive pressure constants, and x_1, x_2, etc., the mole fractions, for all gases present in the equilibrium mixture. M is the modulus of logarithms, 0.43429 . . ., p is the pressure in atmospheres (normal) and T is the absolute temperature ($t° + 273.13$).

At zero pressure $r_e = 3$. At other pressures the sign of the correction depends on the term $(A_{0N}^{1/2} - A_{0H}^{1/2})$, which is $+0.7151163$. Hence the optimum ratio lies at less than 3 for all pressures not zero within which the simplifying assumptions used in deriving Equation 1 are valid.

Although r_e appears on both sides of Equation 6, this does not cause any serious difficulty, as the quantity to be subtracted from 3 is small, and hence the use of an approximate value of r_e on the right-hand side of the equation will lead to a good value. More serious is the fact that x and $\Sigma(x_iA_{0i}^{1/2})$ must be consistent with Equation 4. Hence several trials are necessary to arrive at good numerical values of x and r_e. We have used Equation 6 only for checking the results of other computations.

It appeared somewhat more interesting to calculate the best initial value of the ratio H_2:N_2, which initial ratio we shall designate by r, in a reactant mixture of hydrogen and nitrogen when the nitrogen contains c mole per cent. of argon.

If in such a reactant mixture containing originally no ammonia there is formation of ammonia subject to Equation 2, then the mole fractions of the various gases at any time, for instance at equilibrium, will be related to each other and to r and c by Equations 7

$$\left.\begin{array}{ll} x_{NH_3} = x & x_N = \dfrac{(1 + x)}{(1 + c + r)} - \dfrac{x}{2} \\ x_{Ar} = \dfrac{c(1 + x)}{(1 + c + r)} & x_H = \dfrac{r(1 + x)}{(1 + c + r)} - 3\dfrac{x}{2} \end{array}\right\} \quad (7)$$

These relations (7) will be applied only to the mole fractions at equilibrium

From Equations 4, 5 and 7, log K_p, x_N, x_H and x_{Ar} may be eliminated,

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[13] Gillespie, *J. Math. Phys., Mass. Inst. Tech.*, 4, 84 (1925).

giving an equation between r, x, c, p arid T, containing log K_p^* which is a function of the temperature. From this equation the derivative dx/dr at constant c, p and T may be found and put equal to zero. This gives finally the following equation for the value of the initial ratio r for which x is a maximum at given values of c, p and T.

$$r = 3(1 + c) - \frac{3cx(1 + c + r)}{2(1 + x)} - \frac{2}{M}\left[A_{0\mathrm{N}}^{1/2} - A_{0\mathrm{H}}^{1/2}(1 + c) + A_{0\mathrm{Ar}}^{1/2}c\right] \times \frac{(1 + c + r)}{(1 + x)} x_{\mathrm{N}}x_{\mathrm{H}}\left[38.768 + 128.99\Sigma(x_iA_{0i}^{1/2})\right]\frac{p}{T^2} \qquad (8)$$

For ideal gases the A_0 constants are zero, the last term of Equation 8 vanishes. and we have

$$r = 3 + 3c\,\frac{1 - x - 0.5cx}{1 + x + 1.5cx} \qquad (9)$$

Thus even for ideal gases the best initial ratio is not three when nitrogen cannot be added without adding argon; although of all equilibrium mixtures containing the same mole fraction of argon, the one whose ratio H_2:N_2 is three contains the largest percentage of ammonia.

For any chosen values of c, p and T, Equation 8 may he solved for values of r and x which are also consistent with the mass action and stoichiometric requirements as expressed in Equations 3, 4, 5 and 7. For this purpose an equation may be found of the form $F = 0$, by elimination of log K_p and log K_p^* from Equation 4 by use of Equations 3 and 5. For any chosen value of r, a value of x may then be found by trial which will make the function F reduce to zero. Elimination of the mole fractions x_{N}, x_{H} and x_{Ar} is best made after calculation of their numerical values from Equations 7.

The **Present** Calculations

We have made calculations for the temperature 500°, a series of pressures, and an original mole fraction of argon in the nitrogen, $c = 0.012$. This is about the value of c when nitrogen is made from air and the argon not removed. The function to be reduced to zero is not so formidable as might be expected from the above, once T, p and c have been assigned numerical values, and the numbers have been collected and combined. Thus at 1000 atmospheres the equation we had to solve was

$$F = 0.7985342 + 0.06485898\Sigma(x_iA_{0i}^{1/2}) + 0.10789870\left[\Sigma(x_iA_{0i}^{1/2})\right]^2 + \frac{1}{2}\log x_{\mathrm{N}} + \frac{3}{2}\log x_{\mathrm{H}} - \log x = 0 \qquad (10)$$

subject to the relations (7).

At each pressure the optimum value of r was calculated by Equation 8, using approximate values of the mole fractions, and then an equation such as (10) was solved for x at values of r adjacent to this approximate optimum value. Finally Equation 8 was used to confirm or to locate more precisely the optimum value. The final ratio r_e was also computed from the equation

$$r_e = 3(1 + c) - \frac{2}{M}\left[A_{0N}^{1/2} - A_{0H}^{1/2}(1 + c) + A_{0Ar}^{1/2}c\right]\frac{(1 + c + r_e)}{(1 - x - 0.5cx)}x_N x_H \times \left[38.768 + 128.99\Sigma(x_i A_{0i}^{1/2})\right]\frac{p}{T^2} \qquad (11)$$

The optimum values of r, the initial ratio H_2:N_2, and of r_e, the ratio at equilibrium, are given in Table I. In Table II are given the percentages of ammonia in the equilibrium mixtures at the optimum value of r and also for r = 3. In Table III are given the optimum ratios, and in Table IV the percentages, for the case that no argon is present.

We have thought it of interest to calculate also the percentages at the initial ratios 2 and 4, and also to compare them with the yields that would be expected from the ordinary simple mass action law at the initial ratios 2 and 4 from the percentages for $r = 3$ as given by our improved mass action law. Argon was assumed to be absent.

The yields expected from the ordinary mass action law were obtained by solution of the equation

$$F' = \log p + \log K_p + 1/2 \log x_N + 3/2 \log x_H - \log x = 0 \qquad (12)$$

subject of course to the relations (7), when $\log K_p$ is the correct value of $\log K_p$ found from Equations 4, 5 and 7 for $c = 0$ for the given temperature and pressure.

TABLE I

OPTIMUM RATIOS, INITIAL r AND FINAL r_e OF H_2:N_2, WHEN ARGON ACCOMPANIES THE NITROGEN ($c = 0.012$) AT VARIOUS PRESSURES AND AT 500°

p (atm.)	0	100	300	600	1000
r opt.	3.036	2.99	2.94	2.91	2.92
r_e opt.	3.036	2.99	2.90	2.79	2.72

TABLE II

MOLE PERCENTAGES OF AMMONIA IN EQUILIBRIUM MIXTURES AT VARIOUS PRESSURES AND AT 500° AT OPTIMUM RATIO H_2:N_2 AND AT THE RATIO 3, WHEN ARGON ACCOMPANIES THE NITROGEN

p (atm.)	0	100	300	600	1000
r opt.	0	10.453	25.653	42.083	58.195
$r = 3$	0	10.453	25.649	42.066	58.163

TABLE III

OPTIMUM RATIOS, INITIAL r AND FINAL r_e AT VARIOUS PRESSURES AND AT 500° WHEN ARGON IS ABSENT

p (atm.)	0	100	300	600	1000
r opt.	3	2.96	2.92	2.90	2.91
r_e opt.	3	2.95	2.87	2.76	2.68

TABLE IV

MOLE PERCENTAGES OF AMMONIA IN EQUILIBRIUM MIXTURES AT VARIOUS PRESSURES AND AT 500° AT OPTIMUM RATIO H_2:N_2 AND AT THE RATIO 3, WHEN ARGON IS ABSENT

p (atm.)	0	100	300	600	1000
r opt.	0	10.516	25.809	42.343	58.562
$r = 3$	0	10.516	25.802	42.320	58.523

Table V gives a tabulation of the results of these computations as well as the final ratios r_e.

TABLE V

THE YIELD OF AMMONIA AT VARIOUS PRESSURES AND AT 500° AND AT INITIAL RATIOS $H_2:N_2$ OF 2, 3 AND 4 BY THE IMPROVED MASS ACTION EQUATION, AND THE YIELD AT RATIOS OF 2 AND 4, AS CALCULATED FROM THE YIELD AT 3 BY THE ORDINARY MASS ACTION LAW

	Improved equation			Ordinary mass law	
r	2	3	4	2	4
p	Calculated mole per cent. of ammonia in the equilibrium mixture				
100	10.137	10.516	10.304	10.111	10.321
300	24.690	25.802	24.994	24.529	25.122
600	39.962	42.320	40.174	39.585	40.591
1000	54.020	58.523	53.578	53.551	64.430
	Values of r_e the final ratios $H_2:N_2$				
100	1.840	3	4.305	1.840	4.305
300	1.577	3	5.000	1.581	5.008
600	1.251	3	6.527	1.260	6.594
1000	0.890	3	10.822	0.903	11.414

Discussion of the Results

Whether argon is present in the usual quantities or absent, the optimum initial value of the ratio $H_2:N_2$ passes through a minimum at about 600 atmospheres, at which it is only about 3% less than the value 3; but both the minimum and the smallness of the effect are due to the considerable change in the value of the ratio as a consequence of the extensive formation of ammonia at the higher pressures. The optimum value of the ratio at equilibrium passes through no minimum and reaches a value over 10% less than 3 at 1000 atmospheres.

Although reasons were given above for supposing that the approximate equation used for the calculation should give good results, it would not necessarily follow that pressure derivatives of functions such as the optimum ratio would be furnished correctly, as the terms neglected in deriving the approximate equation would affect the pressure derivatives. Nevertheless in calculations of the Joule–Thomson effect,[14] similar approximations were made and yet a correct slope was obtained of the curve for the inversion temperature *vs.* pressure.

Whether argon is present or not, the maximum mole percentage of ammonia formed at the optimum ratio exceeds the mole percentage formed at $r = 3$ by less than 0.07% of this mole percentage even at 1000 atmospheres. Hence the optimum ratio may safely be taken as 3 for practical purposes, though in point of theory it must be regarded as less.

This practical coincidence of the improved mass action law with the ordinary mass action law is, of course, due to the fact that the value of any

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[14] Beattie, *Phys. Rev.*, 35,643 (1930).

function cannot change rapidly in the neighborhood of its maximum. From Table V it can be seen that if the ordinary mass action law be used to calculate the mole percentage of ammonia when $r = 2$ or 4, from the value given for $r = 3$, it will be found to produce errors which are 0.87 and 1.59% of the correct percentages, respectively, at 1000 atmospheres. Though the pressure here is high, the variation of composition is rather small.

Comparison of Tables II and IV shows that the yield at any pressure is better in the absence of argon. At 1000 atmospheres the improvement is about 0.63% of the yield.

Theoretically, the optimum mixture from nitrogen which contains argon may be improved by adding pure nitrogen. The best initial ratio depends but very slightly on the argon content, being the same for mixtures containing a constant initial mole fraction of argon equal to 0.003 as the figures listed in Table III for zero mole fraction of argon; but the effect on the yield of adding pure nitrogen in this way is small.

Summary

By means of an improved mass action equation, which had previously been found to represent the combined effects of variations of temperature and pressure together with such concomitant variations of composition as necessarily occurred in the displacement of equilibrium, calculations have been made of the effects on the yield of ammonia produced by systematic variation of the ratio of hydrogen to nitrogen. For the temperature 500° and for the pressures 100, 300, 600 and 1000 atmospheres, the optimum values of this ratio, both the initial values and the values at equilibrium, were found for pure hydrogen and nitrogen, as well as for pure hydrogen and atmospheric nitrogen from which the argon has not been removed.

Except at low pressures, the optimum value of the ratio is less than 3. The optimum value of the initial ratio falls to 2.90 at 600 atmospheres, and that of the final ratio at equilibrium to 2.68 at 1000 atmospheres, when no argon is present. The corresponding figures are 2.91 and 2.72 when atmospheric nitrogen is used.

The percentage of ammonia at the optimum ratio exceeds that at the ratio 3 by less than 0.1% of the percentage at 3 in any case.

The presence of argon is deleterious at any pressure. At 1000 atmospheres the yield when pure nitrogen is used is about 0.6% (of its value) greater than when atmospheric nitrogen is used.

For the case of pure nitrogen, the yields of ammonia were also calculated at the values 2, 3 and 4 at each pressure and at 500°. For comparison, the ordinary mass action law was used to calculate the yield of ammonia at each pressure and at the initial values 2 and 4 from the yield at the value 3, with errors which reached at 1000 atmospheres 1.5% of the yield at 3.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE DIRECT DETERMINATION OF SODIUM IN THE PRESENCE OF ALUMINUM AND CHROMIUM

BY EARLE R. CALEY AND DARRELL V. SICKMAN

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The possibility of determining small amounts of sodium in the presence of large amounts of aluminum and chromium is of special interest due to the difficulties involved in the accurate separation of sodium from these elements. When aluminum and chromium are precipitated in the usual manner as hydroxides with the subsequent determination of sodium in the filtrate the results are far from satisfactory even with careful manipulation. Other methods of separation have been proposed but these likewise leave much to be desired. Since a direct analytical method is always desirable for the estimation of small amounts of a given element, the following experiments were performed to determine whether or not the magnesium uranyl acetate method for sodium could be applied satisfactorily to this problem.

General Procedure

In the experiments with pure salts, known volumes of standard sodium solution were added to solutions of known amounts of aluminum and chromium salts and, after evaporation to small volume, the sodium present was determined by the direct magnesium uranyl acetate method for sodium previously described.[1] The technique given in the first paper in this series was followed except for the following variations which further experience with the method has shown to be advisable. Where sulfates are present, which was the usual case in these experiments, precipitates should first be washed with two or three 5-cc. portions of reagent in order to prevent any precipitation of metallic sulfates by the alcoholic washing fluid. Experiment has shown that it is preferable to wash the sodium precipitate with a wash liquid prepared by freshly saturating 95% alcohol with the triple acetate precipitate rather than to wash with pure 95% alcohol and then apply a washing correction, since the latter varies with the amount of precipitate present and with the rapidity of washing. An important point to be noted is that the quantities of salts given in the original formula for the magnesium uranyl acetate reagent referred to the ordinary grades of uranyl acetate and magnesium acetate then obtainable on the market, the latter salt being in the form of so-called "dried" crystals containing less than the theoretical amount of water of hydration. This latter material has been found to differ in composition depending upon its source and since it has now been found possible to obtain clear crystallized magnesium acetate containing the theoretical percentage of water, it is preferable to

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[1] Caley and Foulk, THIS JOURNAL, 51, 1664 (1929).

use this salt in the preparation of the reagent. Based on the employment of salts containing the theoretical percentage of water of hydration the formula of the reagent has been modified to read as follows.

SOLUTION A		SOLUTION B	
Uranyl acetate ($2H_2O$)	90 g.	Magnesium acetate ($4H_2O$)	600 g.
Glacial acetic acid	60 g.	Glacial acetic acid	60 g.
Water	to 1000 cc.	Water	to 1000 cc.

Prepared on this basis more uniform and satisfactory results are obtained.

Materials

Standard Sodium Chloride Solution.—This solution, used as the basis of the experiments, was made by dissolving 2.5418 g. of the purified and carefully dried salt in water and making the solution up to one liter. Each cubic centimeter of this solution contained 0.0010 g. of sodium.

Aluminum Sulfate.--Since it was not found possible to obtain a sample of this salt that did not contain appreciable quantities of sodium, the material had to be especially prepared. For this purpose a quantity of U. S. Bureau of Standards melting point aluminum was dissolved in dilute sulfuric acid and $Al_2(SO_4)_3 \cdot 18H_2O$ was crystallized from this solution and dried in the usual way. The salt thus prepared gave no flame test for sodium.

Aluminum Chloride.—There was used an exceptionally pure commercial material that contained no sodium as determined by the flame test.

Chromium **Sulfate.**—Kahlbaum's $Cr_2(SO_4)_3 \cdot 5H_2O$ was used. The sample employed contained a slight amount of sodium as determined by the flame test and by blank determinations, but the blank was sufficiently small to permit the use of the material in these experiments. The chromium content of the salt was checked and it was found to correspond nearly to the value required by theory.

Ammonium Sulfate.—For experiments on the effect of ammonium salts on the determination of sodium in sulfate solution there was used a sample of "C. P." salt that gave no flame test for sodium.

The Determination of Sodium in **the** Presence of Aluminum.—In the experiments shown in Table I the calculated amount of pure aluminum sulfate was added to the measured volume of standard sodium solution and the resulting solution was brought to a volume of from five to six cubic centimeters. The reagent was then added and the determination made in the usual way. In cases where 0.500 g. of aluminum was present, it was found necessary to add the reagent to the hot solution for salts separated on cooling due to their high concentration, but since the mixture was rapidly brought to the temperature for precipitation this variation did not affect the determinations. **A** similar set of experiments made with aluminum chloride gave like results. In neither case was it found that the presence of the aluminum salts resulted in the separation of any undesirable phase or otherwise influenced the practical accuracy of the sodium determinations, although duplicate values as shown by the weights of precipitates failed to agree as well as similar determinations made with sodium present alone.

TABLE I

DIRECT DETERMINATION OF SODIUM IN THE PRESENCE OF ALUMINUM IN SULFATE SOLUTIONS

Aluminum present, g.	Volume of reagent, cc.	Weight of precipitate, g.	Sodium present, g.	Sodium found, g.	Difference, g.
0.500	250	1.6576	0.0250	0.0264	+0.0004
.500	200	1.6464	.0250	.0252	+ .0002
.200	250	1.6526	.0250	.0253	+ .0003
.200	250	1.6304	.0250	.0249	− .0001
.500	125	0.6631	.0100	.0101	+ .0001
.500	125	.6541	.0100	.0100	.0000
.200	125	.6577	.0100	.0100	.0000
.200	125	.6500	.0100	.0099	− .0001
.500	50	.0657	.0010	.0010	.0000
.500	50	.0659	.0010	.0010	.0000
.200	25	.0550	.0010	.0008	− .0002
.200	25"	.0645	.0010	.0010	.0000
.200	25[a]	.0669	.0010	.0010	.0000
.500	100	No ppt.	None	None	......

[a] In these two samples the solutions were evaporated to a volume of 3 cc. before adding the reagent.

The Determination of Sodium in the Presence of Chromium.—The results from a similar series of experiments in which chromium was present are shown in Table II. Since the chromium sulfate used did contain a small percentage of sodium (0.026% as determined by averaging a series of closely agreeing blank experiments) a corresponding correction was made

TABLE II

DIRECT DETERMINATION OF SODIUM IN THE PRESENCE OF CHROMIUM IN SULFATE SOLUTIONS

Chromium present, g.	Volume of reagent, cc.	Corr. wt. of precipitate," g.	Sodium present, g.	Sodium found, g.	Difference, g.
0.500	250	1.6301	0.0250	0.0249	−0.0001
.500	250	1.6362	.0250	.0250	.0000
.200	250	1.6438	.0250	.0252	+ .0002
.200	250	1.6331	.0250	.0250	.0000
.500	125	0.6544	.0100	.0100	.0000
.500	125	.6538	.0100	,0100	.0000
.200	125	.6613	.0100	.0101	+ .0001
.200	125	.6591	.0100	.0101	+ .0001
.500	25	.0548	.0010	.0008	− .0002
.500	25	.0552	.0010	.0008	− .0002
.200	25[b]	.0609	.0010	.0009	− .0001
.200	25[b]	.0624	.0010	.0010	.0000

[a] Blank of 0.0387 g. deducted from weight of each precipitate when 0.500 g. of chromium was present and blank of 0.0155 deducted when 0.200 g. of chromium was present.

[b] In these two samples the solutions were evaporated to 3 cc. before adding reagent.

in the determined weight of each precipitate, a procedure justified by the resulting consistency of the values thus obtained and by the fact that in separate experiments solutions of chromium salts free from sodium gave no precipitate with the reagent. The results show that chromium, in sulfate solution at least, does not affect the practical accuracy of the direct sodium determination.

The Influence of Ammonium Salts in Sulfate Solutions.—Since ammonium salts are liable to be present in actual determinations, it was thought advisable to determine the effect of rather high concentrations of ammonium salts, especially in sulfate solutions, this usually being the case in direct sodium determinations involving aluminum or chromium. It was found that moderate to high concentrations of both sulfate and ammonium sometimes resulted in the precipitation of the phase $(NH_4)_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ along with the triple acetate precipitate. Experiments on this point (Table III) showed that such concentrations of ammonium and sulfate as can ordinarily be present in 5 cc. of test solution do not result in the precipi-

TABLE III

INTERFERENCE OF AMMONIA SALTS WITH SODIUM DETERMINATIONS IN SULFATE SOLUTION

Aluminum present, g.	Chromium present, g.	Ammonium present, g.	Sulfate present, g.	Volume of reagent, cc.	Sodium present, g.	Key to amount and composition of precipitate[a]
0.200	None	0.500	2.400	25	None	II
.200	None	.500	2.400	50	None	III
.200	None	.500	2.400	100	0.0100	IV
.200	None	1.000	3.731	25	None	I
.200	None	1.000	3.731	50	None	II
.200	None	1.000	3.731	100	None	III
.200	None	1.000	3.731	100	0.0100	IV
.500	None	1.000	5.334	25	None	I
.500	None	1.000	5.334	50	None	II
.500	None	1.000	5.334	100	None	III
None	0.200	1.000	3.217	25	None	I
None	.200	1.000	3.217	50	None	III
None	.200	1.000	3.217	100	None	III
None	.200	0.500	1.885	100	0.0100	IV
None	.200	1.000	3.217	100	.0100	IV
None	.500	0.500	2.717	25	None	III
None	.500	.500	2.717	100	None	III
None	.500	1.000	4.048	25	None	I
None	.500	1.000	4.048	50	None	II
None	.500	1.000	4.048	100	None	III

[a] I. Heavy precipitate of $(NH_4)_2SO_4 \cdot MgSO_4 \cdot 6H_2O$. II. Slight precipitate of $(NH_4)_2SO_4 \cdot MgSO_4 \cdot 6H_2O$. III. No precipitate. IV. Pure precipitate of sodium magnesium uranyl triacetate giving quantitative results for the amount of sodium present.

tation of this undesirable phase providing a sufficient volume of reagent is used. The precipitation of this double salt is, of course, not peculiar to sulfate solutions containing aluminum and chromium but is a general effect governed by the concentration of magnesium, ammonium and sulfate in the solution obtained by mixing test solution and reagent. In general this source of error may be avoided safely by keeping the ammonium salt concentration down to a minimum and using an ample volume of reagent when making direct sodium determinations in sulfate solution. When working with sulfate solutions containing aluminum or chromium it is desirable on another account to keep the ammonium concentration down to a minimum since the ammonium alums are difficult to keep in solution when evaporating to the small volume required by this procedure for sodium. In working with chloride solutions containing aluminum or chromium no particular precautions need be taken in regard to the ammonium salt concentration.

Applications.—In addition to the experiments detailed above, a number of determinations of sodium have been made in commercial samples containing aluminum or chromium, including metallic aluminum, minerals and salts. Satisfactory results have been obtained in these cases, showing that the direct method for sodium may be safely applied to a diversity of materials containing these elements.

Summary

1. It has been shown that the direct magnesium uranyl acetate method for sodium is applicable in the presence of aluminum and chromium.

2. The undesirability of having a high concentration of ammonium salts when making direct sodium determinations in sulfate solution has been pointed out.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

THE MELTING CURVE OF SODIUM CHLORIDE DIHYDRATE. AN EXPERIMENTAL STUDY OF AN INCONGRUENT MELTING AT PRESSURES UP TO TWELVE THOUSAND ATMOSPHERES

BY L. H. ADAMS AND R. E. GIBSON

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Under atmospheric pressure sodium chloride dihydrate melts incongruently at 0.1°, forming solid sodium chloride and a saturated solution of that salt. Below this temperature the dihydrate is the stable solid phase in contact with a saturated solution of sodium chloride, although it exhibits such reluctance to appear that special methods are necessary to bring about its formation. A study of the system $NaCl-H_2O$, at 25° and under high pressure, which is being undertaken by one of us, required an answer to the question—at what pressures, if any, is $NaCl{\cdot}2H_2O$ the stable phase at 25°, a question which could best be answered by a determination of the influence of pressure on the melting point of the dihydrate.

A detailed study of this problem was also of interest as an example of the course of the melting curves of substances melting with decomposition. Although such substances are numerous, only a few such as $Na_2SO_4{\cdot}10H_2O$,[1] $Cd(NO_3)_2{\cdot}4H_2O$,[2] $Ca(NO_3)_2{\cdot}4H_2O$,[2] $CaCl_2{\cdot}6H_2O$[3] have been examined under pressure and none under pressures greater than 3 kilobars.[4] In the case of $Na_2SO_4{\cdot}10H_2O$ there is a maximum on the melting curve in the neighborhood of 500 bars, but in other cases no maxima were realized experimentally.

In this paper we shall give an account of the experimental determination of the following data about the transition point of sodium chloride dihydrate: the volume change at atmospheric pressure; the temperature of the transition point up to pressures of about 12 kilobars; and the volume changes which accompany the inversion at these pressures. We shall also calculate the heat of transition both from the melting curve under pressure and from the solubility curves at atmospheric pressure.

Experimental

Sodium chloride dihydrate, as has been mentioned, exhibits great reluctance to crystallize from solution, but, following a suggestion of Meyer-

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[1] G. Tammann, *Z. physik. Chem.*, *46*, *818* (1903); E. A. Block, *ibid.*, 82, 429 (1913).

[2] Puschin, *J. Russ. Phys.-Chem. Soc.*, 37, *382* (1905); M. Hasselblatt, *Z. anorg. allgem. Chem.*, 119, 320 (1922).

[3] Tammann, "Kristallisieren und Schmelzen," Leipzig, 1903.

[4] 1 bar = 10^6 dynes per sq. cm.; 1 kilobar = 10^3 bars (approx. 1000 atmospheres). See Adams and Gibson, J. *Wash. Acad. Sci.*, 20, 213 (1930).

hoffer and Saunders,[5] we found that it was possible to prepare the pure hydrate easily and in any desired quantity by cooling a solution of sodium chloride, saturated at room temperature, to below −5° and throwing on the surface of the solution a small amount of carbon dioxide snow. Immediately a cloud of fine crystals of the dihydrate appeared in solution. Below −5° the solubility of sodium chloride is much greater than that of $NaCl\cdot 2H_2O$, so that introduction of solid sodium chloride into the cold bath of dihydrate crystals results in immediate solution of anhydrous salt and precipitation of more dihydrate.

The mother liquor was removed from the crystals by decantation and suction through a chilled filter.

Change in Volume Accompanying the Melting of $NaCl\cdot 2H_2O$ at One Atmosphere.—It was difficult to dry the dihydrate completely; hence the dilatometer (a glass one of the usual kind) was filled with the moist salt. Any air was carefully pumped out and xylene introduced as index liquid. During all these operations the temperature of the salt was kept below 0°. When filled and sealed up the dilatometer was immersed in a cold bath and the heights of the meniscus of the xylene in the capillary at different temperatures were read. The changes in height of the meniscus, corrected for temperature of the capillary and irregularities in the bore, were converted to volume changes and plotted against temperature. From the curve was read the increase in volume accompanying the decomposition at 0.1°, which is the mean of the inversion temperatures as given in the literature (0.15°) and as determined by us (0.05°).

After each experiment the amounts of anhydrous sodium chloride and water contained in the dilatometer were determined, and hence with the knowledge of the solubility of sodium chloride at the inversion point we could calculate the actual amount of solid $NaCl\cdot 2H_2O$ whose volume change on melting was measured.

If A is the weight of salt and water and B the weight of salt in the dilatometer, x_2 and x_0 the weight fractions of sodium chloride in the saturated solution and the solid dihydrate, respectively, at 0°, and m_2 the unknown weight of solid dihydrate before inversion, we find that

$$m_2 = \frac{B - Ax_2}{x_0 - x_2}$$

x_2 was taken from the data of Berkeley[6] as 0.2633 and x_0 is 0.6187. Two experiments were performed, m_2 being 9.628 g. in the first and 8.846 in the second.

The results gave 0.0362 and 0.0377, or an average of 0.037 cc./g. of $NaCl\cdot 2H_2O$ as the increase in volume accompanying the transition, $NaCl\cdot 2H_2O \longrightarrow NaCl + \text{Satd. Soln.}$ at 0.1°. By taking Berkeley's value, 1.2090,

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[5] Meyerhoffer and Saunders, *Z. physik. Chem.*, 31, 381 (1899).

[6] Berkeley, *Phil. Trans.*, 203, 189 (1904).

for the density of a saturated salt solution at 0°, and the density of sodium chloride as 2.168,[7] we calculated that the density of $NaCl \cdot 2H_2O$ at 0° is 1.630 g. per ml.

A few qualitative observations on the speed of the reaction may be noted here. The reaction did not proceed at any appreciable rate until the temperature was 1–2° above the inversion point, and even then the rate was slow. It required over an hour for the reaction to go to completion at a temperature of 4°. At constant temperature the reaction accelerated as more and more anhydrous salt was formed, reaching a maximum speed when about half the material had inverted.

The Effect of Pressure on the Transition Point. (a) Low-Pressure Experiments.—In order to examine the initial portion of the p–t curve of the melting of $NaCl \cdot 2H_2O$, a sample of the hydrate was enclosed in the bomb of the pressure dilatometer apparatus whose description has already been published in detail.[8]

The bomb was immersed in a low-temperature bath, a suitable pressure generated, and the system, bomb and pressure gage tightly closed. The criterion of the inversion proceeding in any direction was steady change of pressure at constant temperature. At first the temperature of the bath was raised to a point where rise of pressure indicated that the hydrate was decomposing. The temperature was then lowered to a point where falling pressure showed that re-formation of hydrate was taking place. After that the temperature was raised by short intervals, the trend of the pressure change being carefully observed until it was possible to shut the equilibrium temperature within limits of ±0.25°. The results are given in Table I. In this way the points at 180, 270, 550 and 850 bars on the curve in Fig. 2 were obtained. These points established the initial slope of the p–t curve for $NaCl \cdot 2H_2O$ to our satisfaction.

TABLE I

MELTING POINTS OF $NaCl \cdot 2H_2O$ AT LOW PRESSURES

Expt.	Temp., °C.	Pressure, bars	Uncertainty, °C.
DW447	0.05	1	±0.05
DW445	1.0	180	± .1
DW425	2.0	270	± .1
DW439	3.6	535	± .2
DW429	3.7	570	± .25
DW431	5.4	830	± .2
DW435	5.4	855	± .2

(b) High-Pressure Experiments.—Determination of points on the melting curve of $NaCl \cdot 2H_2O$ at high pressures required a different experimental technique. The high-pressure apparatus used in this Laboratory

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[7] DeFoe and Compton, *Phys. Rev.*, [2] *25*, 618 (1925).

[8] Kracek and Gibson, *J. Phys. Chem.*, *34*, 190 (1930).

has already been described.[9] It consists essentially of a very heavy-walled steel cylinder or bomb in which the system under investigation is immersed in n-butyl ether, a liquid selected because of its high freezing pressure. A special type of leak-proof piston is forced into the open end of the cylinder and hydrostatic pressure generated in the butyl ether. The pressure is measured by an electrical resistance gage.

The apparatus is large and, although protected from minor temperature variations by an insulating housing, is approximately at the temperature of the room. The apparatus could be held constant for a day at temperatures between 17 and 26°, and by following a special procedure it was possible to determine the equilibrium pressures at these temperatures. A glass tube (see Fig. 1) was filled with slightly moist dihydrate, placed in a somewhat larger steel tube filled with butyl ether and kept for half an hour in a eutectic mixture of chloroform and carbon dioxide (approx. −80°). The tubes and their contents were introduced into the bomb and the pressure was raised as expeditiously as possible to the highest value. Five minutes elapsed between the removal of the capsules from the freezing mixture and the pressure on the dihydrate exceeding 7 kilobars. From auxiliary experiments at atmospheric pressure it was found that very little inversion of the salt would take place during the interval required for raising the pressure. A series of readings of pressure and piston displacement was taken when the apparatus came to temperature equilibrium. Rise or fall of pressure, temperature and piston displacement being constant, indicated decomposition or forma-

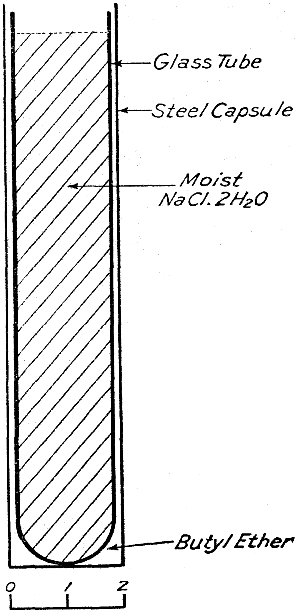

Fig. 1.—Arrangement of the material for the high-pressure experiments.

TABLE II

MELTING POINTS OF $NaCl\cdot 2H_2O$ AT HIGH PRESSURES

Expt.	Temp., °C.	Pressure, bars	Uncertainty, bars
AP503	17.15	3620	± 20
AP505	21.21	5190	± 25
AP513a	23.77	6740	± 50
AP517	23.79	6731	± 50
AP498	24.30	7220	± 50
AP513b	24.66	7500	± 40
AP513c	25.17	8250	±100
AP525	25.10	11800	±250

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[9] (a) Adams, Williamson and Johnston, THIS JOURNAL, 41, 12 (1919); (b) Adams and Gibson, Proc. *Nat. Acad. Sci.*, 15, 713 (1929).

tion of the dihydrate and by prolonged observation we were able at temperatures up to 25° to estimate the inversion pressure to within the limits of error given in Col. 4 of Table II. It was also possible to make reliable estimates of the change in volume on inversion at these higher pressures. The results are recorded in Table II and the complete melting curve is illustrated in Fig. 2.

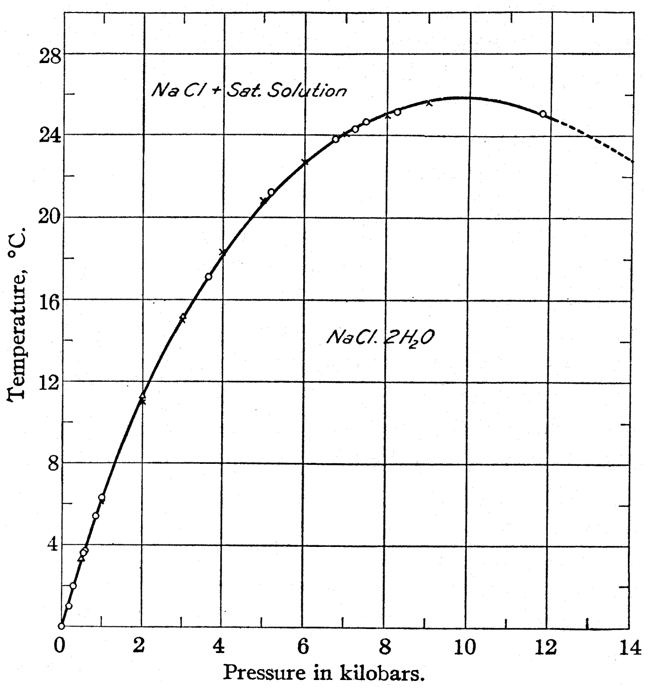

Fig. 2.—The influence of pressure on the incongruent melting of $NaCl{\cdot}2H_2O$.

Change in Volume at Higher Pressures.—At higher pressures the volume change on inversion, Av, which is proportional to the slope of the *p–t* curve, becomes very small. Even with the volume of the system under pressure reduced to a minimum, we had difficulty in fixing the inversion pressure and temperature at the higher pressures, and, indeed, it was almost impossible to obtain results by direct measurement between 8 and 11 kilobars. As one of the most interesting features of this work was the investigation of the possibility of a maximum on the melting curve, we decided to measure as accurately as possible the difference between the specific volume of $NaCl{\cdot}2H_2O$ and its decomposition products at pressures up to 12,000 bars. The maximum on the melting curve would occur at the pressure where Av is zero. Two methods were used to estimate Av. Method 1 consisted of determining the rise in pressure at constant volume or the increase in volume at constant pressure by direct observations near the actual inversion point at any temperature. Results were obtained in this way below 8 kilobars and are given in the second column of Table III. Method 2, being rather novel and depending on the fact that a mixture of sodium chloride and its saturated solution will remain in a metastable state several thousands of bars above the inversion point, will now be discussed in some detail. The piston displacements for a given amount of dihydrate at pressures from 6 to 12 kilobars were compared with the piston displacements for the decomposition products of the same sample of dihydrate (sodium chloride and saturated solution) at the same pressures obtained at the same temperature in such a way that errors due to hysteresis in the bomb were reduced to a minimum. The procedure may be illustrated by an example. A quantity of $NaCl{\cdot}2H_2O$ was placed in the bomb at 23.3°. The pressure was raised to exactly 12,400 bars and then reduced to 30 bars below 12,000 bars. A pause was made for temperature readjustment, and then the pressure was raised to as near 12,000 bars as possible. A reading of the piston displacement was taken. Similar observations of displacement and pressure at intervals of 1000 bars were made down to 7000 bars. The pressure was now lowered to 5700 bars, which is 500 bars below the inversion pressure at 23.3°. Readings were noted and a rise of pressure which was allowed to go on only for a short time indicated that $NaCl{\cdot}2H_2O$ was decomposing. The pressure was again raised to 12,400 bars and a second series of measurements was taken. The first run was made merely to put the apparatus through a definite hysteresis cycle. At the end of the second series the inversion was allowed to go to completion. Incidentally the rise of pressure at constant piston displacement gave a measure of Δv at 5700 bars.

After the reaction was entirely finished the pressure was again raised to 12,400 bars and a third series of pressures and piston displacements was observed.

This was followed by a fourth series of observations made in exactly the same way. By noting the differences between two successive runs made with the material in the bomb in the same state of aggregation we were able to make corrections for the small systematic difference between two successive series. The differences between the corrected piston displacements before and after the inversion when multiplied by the cross section area of the hole in the bomb and divided by the weight of dihydrate used gave the approximate change in volume per gram accompanying the inversion at pressures from 6 to 12 kilobars. Three experiments were made at temperatures of 23.3, 23.7 and 24°. In each case an additional value of Δv at 6000 bars was obtained by observation of the total rise in pressure during the inversion. In the experiments at 23.3 and 23.7° uncertainty arose as to the exact amount of dihydrate in the bomb. The results were calculated in such a way that the values of Δv at 7000 bars were made equal to that obtained in the experiment at 24°. All the results on volume changes are recorded in Table III.

TABLE III

INCREASE IN VOLUME OF $NaCl\cdot 2H_2O$ ON MELTING AT VARIOUS PRESSURES

Pressure, bars	Δv, cc./g., Method 1	Δv, cc./g., Method 2 1	2	3
3620	0.0165			
5190	.0101			
6000		0.0069	0.0074	0.0071
7000		(.0046)	(.0046)	.0046
7220	.0054			
8000		.0027	.0026	.0027
9000		.0012	.0010	.0006
10000		− .0004	− .0008	− .0009
11000		− .0021	− .0019	− .0024
12000		− .0032	− .0034	− .0036

Discussion of Results

Interpolation Formulas.—Two cubic equations

$$t = 7.047p - 0.7655p^2 + 0.035244p^3 \tag{1}$$

$$t = 0.06 + 6.512p - 0.5529p^2 + 0.06056p^3 \tag{2}$$

were found to express the melting temperature as a function of pressure. The temperature, t, is expressed in degrees centigrade and the pressure, p, is in kilobars. Equation 1 being passed through the points at lower pressures gives more accurately the initial slope of the pressure–temperature curve, but it does not represent the data very well above 4.5 kilobars. Equation 2, we consider, expresses the results accurately between 4 and 8 kilobars. Indeed, it applies very well to atmospheric pressure, which is surprising when it is mentioned that the lowest point used in computing this equation was that at 17.15° and 3.620 kilobars.

In Fig. 2 the circles represent the observed points, the crosses, points calculated from Equation 1, and the triangles, points calculated from Equation 2. Both equations are purely interpolation formulas and are not suited for extrapolation.

Maximum on Melting Curve.—From direct observations of melting we can say definitely that at 8000 bars sodium chloride dihydrate becomes the stable phase in contact with a saturated solution at 25°. The question as to whether the melting curve passes through a maximum and whether at some higher pressure sodium chloride is again stable at 25° may be answered from considerations of the volume changes. In Fig. 3 we have plotted points representing Δv per gram at different pressures as measured by our first method (triangles), and as determined by the second method (circles). The two series are fairly consistent, although the second method appears to give values which are somewhat lower than those given by the first. The curve passed through these points cuts the pressure axis at 9500 bars, showing that the melting curve passes through a maximum at this pressure. It should be mentioned that the values of Δv at the higher pressures are calculated on the assumption that the effect of temperature on the change in volume during the inversion is negligible when compared with the effect of pressure.

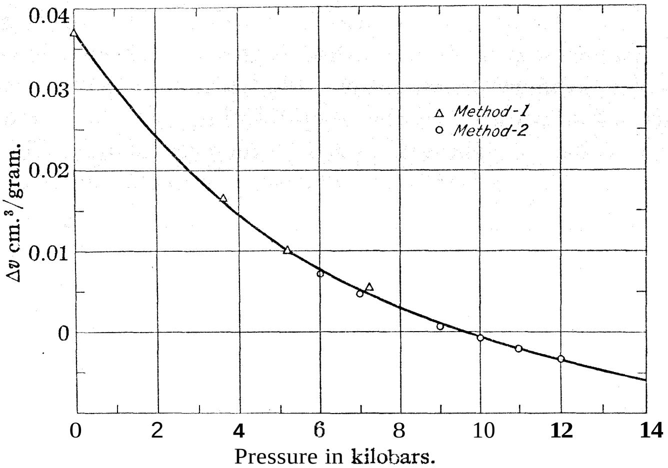

Fig. 3.—Volume change accompanying the melting of 1 g. of $NaCl \cdot 2H_2O$ at various pressures. Above 9500 bars the volume change is negative.

Confirmation of the maximum on the melting curve was obtained by direct observation of the decomposition of $NaCl \cdot 2H_2O$ at 12,500 bars and 25.1'. The pressure on the sample was first raised to 12,500 bars and dropped to 10,000 bars, where it was held until equilibrium was established. The pressure was then raised by steps of 500 bars and at each pause was carefully watched and its trend noted. Below 12,000 bars and above 10,000 bars the creep of pressure after the primary rise was always upward—there was no tendency to fall. This phenomenon will be referred to later. At 12,000 bars the pressure drifted down slowly but steadily and in the course of four hours dropped 80 bars. That this drop was due to the decomposition of $NaCl \cdot 2H_2O$ was shown when the pressure was finally lowered to 7000 bars (1000 bars below the low-pressure equilibrium value at 25') and the total rise at constant volume was about one-third that which would be obtained from the particular sample of uninverted dihydrate. As the pressure rose at constant volume at 11,500 bars, we were able to place the pressure coördinate of the melting curve at 25.1' between 11,500 and 12,000 bars.

The Compressibility of $NaCl \cdot 2H_2O$.—The volume of sodium chloride at any pressure is known from compressibility measurements,[9a] and recently the specific volumes of saturated sodium chloride solutions have been determined to 12 kilobars.[10] As we have measured around 25° the differences in volume between $NaCl \cdot 2H_2O$ and its decomposition products, it is possible to calculate the specific volume of the hydrate at pressures between 6 and 12 kilobars. It is assumed that the solubility of sodium chloride is not greatly altered by pressure in this range. The results are recorded in Fig. 4 where v_0, the specific volume, is plotted against the pressure. The slope of this curve, when divided by the specific volume of $NaCl \cdot 2H_2O$ at ordinary pressure, gives the fractional decrease in volume per bar increase of pressure, or the compressibility β. The average value of β between 6 and 12 kilobars is 4.8×10^{-6} reciprocal bars. This may be compared with 3.6×10^{-6}, the value of β for sodium chloride at 9 kilobars.

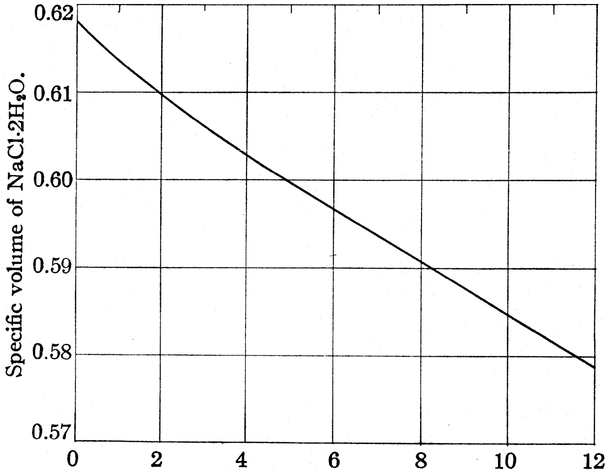

Fig. 4.—The specific volume of $NaCl \cdot 2H_2O$ as a function of pressure.

Heat of Inversion from the Melting Curve.—The initial slope of the melting curve is shown by Equation 1 to be 7.05° per kilobar. The volume change at atmospheric pressure is 0.037 cc. per gram of $NaCl \cdot 2H_2O$, and hence by the Clausius–Clapeyron equation the heat of fusion per gram, Ah, is 34.4 cal. In the same way, obtaining Av from the curve in Fig. 3 and dt/dp from Equation 2, we find that at 5 and 7 kilobars Ah is 36.4 and 33.1, respectively. The heat of fusion is not greatly influenced by pressure—a fact which is in accord with Bridgman's[11] observations on various materials.

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[10] Adams, unpublished data.

[11] Bridgman, *Phys. Rev.*, 3, 190 (1914).

Secondary Increase of Pressure.—On all occasions when a charge of dihydrate was held at a pressure and temperature in the vicinity of the maximum on the melting curve a very curious phenomenon was observed. The pressure had been raised to somewhat above 10,000 bars, and, contrary to what was expected, it continued to drift slowly *upward* for an hour or more, the total increase of pressure being as much as 20 bars. The normal behavior of a system the pressure of which has just been increased is, of course, to show at first a small decrease of pressure—even in a pressure-tight apparatus. The immediate cause of this decrease may be the cooling subsequent to the heating by compression, or, in a multi-phase system, the transformation of one phase to another in accordance with the conditions of equilibrium. Similarly, a decrease of pressure is usually followed by a secondary increase. In the simple case of a mixture of solid and liquid in equilibrium an increase of pressure causes the production of more solid (in rare instances more liquid), and since this is accompanied by a decrease of volume, the pressure falls, finally coming back, if the primary increase is not too great and the substance is a pure material, exactly to the original pressure.

The abnormal behavior of the sodium chloride dihydrate, which at first seemed very puzzling, may be explained as follows. Suppose that a mixture of the dihydrate and its decomposition products is held at a temperature and pressure corresponding to the point *O* in Fig. 5, and that the pressure on the system is suddenly increased. The temperature will increase with the pressure, approximately isentropically, as shown by the dotted line. The material will then begin to cool, and the secondary pressure change will be the sum of two effects: (1) the effect due to cooling and (2) the effect due to transformation from one form to the other. In the present case the problem is much simplified because the inversion takes place relatively slowly so that during the time required for the temperature to return to its original value (about five minutes) very little of the material has changed its state. On the diagram, therefore, the temperature and pressure reach the point *a* while there is still present a mixture of the dihydrate and its decomposition products. Since at this point dihydrate is the stable phase, solution and salt will react to form dihydrate, which under the given conditions has the smaller volume, and hence the pressure will fall. Suppose, on the

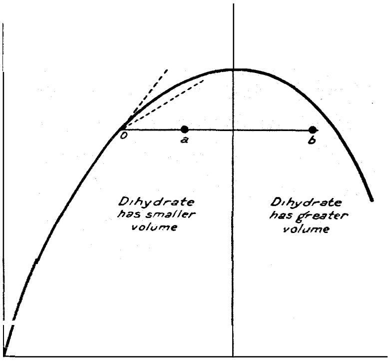

Fig. 5.—Diagram to accompany explanation of secondary increase of pressure.

other hand, that starting again with a mixture at O, the pressure is suddenly increased, attaining at the same temperature the pressure indicated by b. Here, as before, dihydrate is the stable phase, and more will be formed, but the pressure being now beyond the maximum, the dihydrate occupies more volume and the pressure therefore will rise. A secondary increase of pressure has been discussed by Tammann[12] in connection with the existence of maximum melting points, but Bridgman in a careful analysis of the problem points out that the conditions of equilibrium in a system make it impossible for Tammann's secondary increase of pressure to occur. According to Bridgman,[13] in a system composed of phases in equilibrium, and each in condition of internal stability, thermodynamical considerations require that the secondary pressure reaction be a decrease rather than an increase. That this result, however, does not contradict the opposite conclusion obtained as above from elementary principles becomes apparent when we recall that Bridgman's equation is valid only for *infinitesimal* changes and is not necessarily applicable to the *finite* changes here under discussion. It is only because we have increased the pressure a considerable distance beyond the equilibrium curve and into that part of the field which lies beyond the maximum that the secondary increase of pressure occurs. Expressed in other terms: we are here dealing with a non-equilibrium process, whereas the thermodynamical equations refer only to equilibrium states and their immediate vicinity. It should be noted that the above considerations apply equally well to the melting curve of a substance which does not decompose at its melting point.

Heat of Inversion from the Solubility Curves.—No direct measurements of the latent heat of the incongruent melting of $NaCl \cdot 2H_2O$ are available but it is possible to calculate this heat of inversion from solubility measurements of sodium chloride in water and from the known values of the chemical potential of sodium chloride in aqueous solution. The relation is

$$\Delta h = T(b_3 - b_2)\frac{\partial \mu_2}{\partial x_2}\frac{x_0 - x_2}{1 - x_2} \qquad (3)$$

Here Ah is the heat absorbed, when one gram of $NaCl \cdot 2H_2O$ inverts to *a* mixture of sodium chloride and saturated solution of sodium chloride in water, T is the absolute temperature, x_0 is weight fraction of sodium chloride in $NaCl \cdot 2H_2O$, x_2 is the weight fraction of sodium chloride in the saturated solution which is in equilibrium with sodium chloride and $NaCl \cdot 2H_2O$, b_3 is the slope dx_2/dT of the solubility curve for $NaCl \cdot 2H_2O$ as the solid phase, b_2 is dx_2/dT for the solubility curve with sodium chloride as the solid phase, and μ_2 is the chemical potential of Gibbs (or partial free energy of Lewis) referred to one gram of sodium chloride in solution.[14] In the expression

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[12] G. Tammann, "Kristallisieren und Schmelzen," p. 87.

[13] P. W. Bridgman, *Phys. Rev.*, 3, 192 (1914).

[14] If it is desired to express the above equation in terms of activity and mole frac-

$\partial\mu_2/\partial x_2$ the temperature is constant. The derivation of the equation will be given in another paper from this Laboratory.

From a careful plot of the solubility data of sodium chloride in water as given in the "International Critical Tables," b_3 is found to be 0.00138 and b_2 0.00001. The solubility of sodium chloride, x_2, at the inversion point is 0.263, and x_0 is 0.619. The absolute temperature of the inversion, T_1, is 273.2°, and the value of $\partial\mu_2/\partial x_2$, as determined from freezing point, e. m. f., solubility and vapor-pressure data, and corrected to $t = 0.1°$, is taken as 165 calories. Substituting these numerical quantities in Equation **3** we have

$$Ah = 30 \text{ cal.}$$

for the heat absorbed by the incongruent melting of one g. of $NaCl{\cdot}2H_2O$.

This result is to be compared with 34 cal., the value obtained from the initial slope of the p–t curve and the volume change at $p = 1$. The agreement is none too close, but considering the complexity of the calculation, and the large variety of data involved, it is an interesting confirmation. Probably about equal weight should be given to the value of ***Ah*** obtained from the solubility curve and that derived from the initial slope of the melting curve.

Summary

The temperature of the incongruent melting of $NaCl{\cdot}2H_2O$ has been determined up to 12,000 bars (or c. g. s. atmospheres) by direct measurement and also indirectly from measurements of the volume changes. The melting curve starts at 0.1' at atmospheric pressure with an initial slope of 7.05' per kilobar. The slope decreases rapidly with increasing pressure, finally becoming zero, so that the curve passes through a maximum at 9500 bars and 25.8'.

The volume change was measured at one bar in a dilatometer, and at various pressures up to 12,000 bars by two different methods. From the volume change and slope of the melting curve the heat of fusion at several pressures was calculated. The density of $NaCl{\cdot}2H_2O$ at 0.1° and one bar

tions, this can be done by making use of the relation $d\overline{F}_2 = M_2 d\mu_2 = RT\, d \ln a_2$ at constant temperature, in which $\overline{F}_2$ is the partial molal free energy, M_2 the formula weight, a_2 the activity of component 2, and R is the gas constant. The transformed equation is

$$\Delta H = 3RT^2(B_3 - B_2)\,\frac{d \ln a_2}{dX_2}\,\frac{X_0 - X_2}{1 - X_2}$$

in which ΔH is the heat observed when one mole of $NaCl{\cdot}2H_2O$ inverts, X_2 is the mole fraction of sodium chloride in the equilibrium solution, X_0 is the mole fraction of sodium chloride in $NaCl{\cdot}2H_2O$, B_3 and B_2 are the values of dX_2/dt along the $NaCl{\cdot}2H_2O$ and sodium chloride curves, respectively, and a_2 is the activity of sodium chloride in solution. Moreover, the activity coefficient γ may be used in place of a_2 by making the substitution, $d \ln a_2/dX_2 = \nu\, d \ln (m\gamma)/dX_2$, ν being the number of ions into which one molecule of the solute is assumed to dissociate.

was found to be 1.630, and its mean compressibility between 6000 and 12,000 bars at about 22°, 4.8×10^{-6} per bar. A method for calculating the heat of fusion from solubility data gives a value which is in fair agreement with that determined from the initial slope of the melting curve, the average value being 32 cal. per g. of $NaCl\cdot 2H_2O$.

A secondary pressure increase, that is, a continued rise of pressure following a sudden increase, was observed at pressures near the maximum on the curve, and an explanation is given for this phenomenon.

WASHINGTON, D. C.

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

THE SEPARATION OF YTTERBIUM BY ELECTROLYTIC REDUCTION.

OBSERVATIONS ON THE RARE EARTHS. XXXVI

BY ROBERT W. BALL[1] WITH L. F. YNTEMA

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Recently it was found that europium can be separated from a mixture of samarium, europium and gadolinium chlorides by electrolytic reduction in acid solution in the presence of the sulfate ion.[2] Europous sulfate, $EuSO_4$, precipitated as a white, finely crystalline compound, stable when heated in air at 65° and insoluble in dilute acids. It was readily oxidized by dilute nitric acid.

In 1929 Klemm and Schüth[3] reported the preparation of ytterbous chloride, $YbCl_2$, similar to samarous chloride, $SmCl_2$,[4,5] and europous chloride, $EuCl_2$[6,7] by treatment of ytterbium oxide, Yb_2O_3, with a stream of Cl_2–S_2Cl_2 at 600–620°.

These facts suggested the possibility of separating ytterbium from the other rare earths of the yttrium group by electrolytic reduction in the presence of the sulfate ion.

Experimental

I. Electrolysis of Rare Earths with Low Ytterbium Content.—Ten grams of pink yttrium group oxides, containing yttrium and erbium with small percentages of thulium and ytterbium, were dissolved in hydrochloric

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[1] An extract from a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate School of the University of Illinois.

[2] Yntema, THIS JOURNAL, 52, 2782 (1930).

[3] Klemm and Schüth, Z. *anorg. allgem. Chem.*, 184, 352 (1929).

[4] Matignon and Cazes, *Compt. rend.*, 142, 83 (1906).

[5] Jantsch, Rüping and Kunze, Z. *anorg. allgem. Chem.*, 161, 210 (1927).

[6] Urbain and Burion, *Compt. rend.*, 153, 1155 (1911).

[7] Jantsch, Alber and Grubitsch, *Monatsh.*, 53, 54, 305 (1929).

acid. The excess acid was evaporated, the solution diluted to 400 cc. and 4 cc. of sulfuric acid (sp. gr. 1.84) was added.

This solution was put into the cathode compartment of an electrolytic cell with a mercury cathode.[2] The anode compartment was filled to the same level with approximately 0.05 N hydrochloric acid. A current of 0.1 ampere, corresponding to a current density at the cathode of 0.025 amp./sq. cm., was used. The voltage drop between electrodes was 110 volts.

The solution was electrolyzed almost continuously for one hundred and ten hours. The only interruptions were during the nights when enough of the hydrogen evolved would get into the salt bridge to shut it off. During the first hour of the electrolysis the solution became dark. This soon cleared up and after thirty-two hours the solution, which was originally pink, had become clear green in color. Visual examination of the solution with a hand spectroscope still showed the absorption spectrum of erbium while there was also general absorption in the red part of the spectrum. At the end of eighty hours a greenish-white crystalline precipitate started to form. At the end of one hundred and ten hours the precipitate was filtered off, washed with boiled distilled water and dissolved in nitric acid. It dissolved in concentrated nitric acid with the evolution of brown fumes, indicating that it was a reduced compound. Any heavy metals with which the precipitate might have become contaminated were removed with hydrogen sulfide. The rare earths were precipitated as oxalate and ignited to the oxide, which was white in color. A qualitative test showed that the anion of the precipitate was sulfate.

Photographs were made of the arc spectra on carbon electrodes of the original mixed oxides and of the oxide from the precipitate.

The more prominent lines on this photograph were examined. The results obtained are shown in Table I.

TABLE I

SPECTRUM LINES

Wave lengths in I. A.	Element	Intensity of line in original	Intensity of line in precipitate	Wave lengths in I. A.	Element	Intensity of line in original	Intensity of line in precipitate
4935.51	Yb	0	7	4422.60	Y	10	1
4900.11	Y	7	1	4398.03	Y	8	2
4883.69	Y	7	1	4374.95	Y or Er	10	5
4854.88	Y	7	1	4358.72	Y	6	1
4823.31	Y	2	0	4309.62	Y	10	4
4786.60	Yb	0	7	4305.97	Yb	0	5
4781.90	Yb	0	7	3933.67	Ca	4	7
4564.00	Yb	0	3	3906.34	Er	4	1
4552.12	Er	3	3	3900.83	Yb	0	5
4527.80	Y	3	1	3472.5	Lu or Yb	4	4
4515.15	Yb	0 -	4	3467.88	Y	3	1
4439.22	Yb	0	8				

From this examination it was concluded that, while the original material contained only 1 or 2% of ytterbium, the precipitate consisted of ytterbium with very little of the other rare earths (estimated at 1 or 2%).

The authors wish to express their appreciation to Mr. P. W. Selwood for his assistance in the examination of the arc spectra of the original and precipitated oxides.

II. Electrolysis of Rare Earths with High Ytterbium Content and Analysis of the Precipitate.—Samples of ytterbium-rich oxide which were white in color and, when dissolved in hydrochloric acid, showed no absorption in the visible region of the spectrum, were also electrolyzed. The same color changes and precipitate formation as noted above took place although much more rapidly than in the solutions containing less ytterbium. When one or one and a half grams of precipitate had formed, the solution was decanted and the precipitate collected on a sintered glass crucible. It was found that the precipitate dissolved slowly if left in contact with the solution with constant evolution of gas. The decanted solution was clear green and bubbles of gas formed through its entire volume. At the end of about fifteen minutes it became colorless and no more gas was evolved.

The precipitate was washed successively with freshly boiled distilled water, alcohol and ether, and heated to constant weight at 72°. It was found that the precipitate gained weight when exposed to air at room temperatures; the crucible was therefore transferred to a glass-stoppered

TABLE II

RESULTS OF ANALYSES OF PRECIPITATES OBTAINED BY ELECTROLYSIS WITH MERCURY CATHODE OF RARE EARTHS WITH HIGH YTTERBIUM CONTENT

		IA	IB	II	IIIB	IIIC
1	Concn. of soln.	5 g. oxide in 200 cc.		10 g. oxide in 100 cc.	(Filtrate from Run III) 10 g. oxide in 100 cc.	Filtrate from Run IIIB
2	Hours. soln. elec.	37		6.5	3.0	5.5
3	Cur. dens., amps./sq. cm.	0.025	0.025	0.165	0.165	0.165
4	Wt. of precipitate, g.	.6585	.4736	.5879	.4595	.3727
5	Weight of Yb_2O_3, g.	.4549	.3215	.4023	.3113	.2388
6	Weight of $BaSO_4$, g.	.5200	.3481	.2969	.3044	.2533
7	Wt. of Yb (calcd. from No. 5), g.	.3996	.2825	.3534	.2735	.2098
8	Wt. of SO_4 (calcd. from No. 6). g.	.2140	.1433	.1222	.1253	.1043
9	Wt. of $YbSO_4$ (7 plus 8), g.	.6136	.4258	.4756	.3988	.3141
10	Weight of H_2O (?) and O_2 (?) (4 minus 9), g.	.0449	.0478	.1123	.0607	0586
11	Mol. ratio SO_4:Yb	.968	.917	.625	.828	.898

weighing bottle before cooling. The analysis was carried out as described in a previous publication.[2] The results are given in Table II.

The ratio of sulfate to ytterbium was always less than unity. It was found that the material which approximated closest to a 1:1 ratio for ytterbium and sulfate was precipitated when the current density was low, the solution was dilute and the hydrogen-ion concentration fairly high. In this investigation no attempt was made to determine the optimum hydrogen-ion concentration for precipitation. The acid concentration in the cathode compartment of the cell at the start of a run was **0.37** N and this was decreased by the electrolysis. Care must be exercised, however, to prevent hydroxide formation through too low acidity. It is supposed that ytterbium is precipitated as $YbSO_4 \cdot xH_2O$, in which the water content is unknown. The fact that the sulfate content is lower than is theoretically correct may be explained by assuming that there is hydrolysis after the precipitation has taken place. It should be pointed out that the completeness of separation is not affected by any change taking place in the precipitate after it has once formed.

It was noticed that ytterbous sulfate was only stable in the acid solution when current was flowing and the cathode was one with a high overvoltage. When the current was shut off, the precipitate slowly dissolved with the evolution of hydrogen. The reaction is probably

$$2YbSO_4 + 2H^+ \longrightarrow 2Yb^{+++} + 2SO_4^{--} + H_2$$

Of particular interest is the green coloration which always appeared when ytterbium salts were reduced. Examination with a hand spectroscope showed no absorption bands, but general absorption in the red. When europium salts were reduced there was no change in color. When ytterbium was present, even if only in small amounts, the green coloration always appeared. It appeared before any precipitate formed and remained as long as the electrolysis was continued. On shutting off the current, or decanting the solution into a beaker, bubbles of hydrogen formed throughout the clear green acidic solution and within fifteen minutes the solution had become colorless. The reaction is probably

$$2Yb^{++} + 2H^+ \longrightarrow 2Yb^{+++} + H_2$$

The ytterbic ion, Yb^{+++}, is colorless, but the ytterbous ion, Yb^{++}, appears to be green.

Attempts to reduce ytterbium, using cadmium or platinum cathodes, were not very successful.

Summary

1. Bivalent ytterbium sulfate may be precipitated from an acid solution by electrolytic reduction in the presence of the sulfate ion.

2. Arc spectrum analysis indicates that ytterbium of 98% purity may

be separated in one operation from mixed yttrium group material containing 2% ytterbium.

3. Analysis of the precipitate showed it to be of variable composition approaching the formula $YbSO_4 \cdot xH_2O$. It is a very light green crystalline compound. It is soluble in dilute acids with the evolution of hydrogen and in nitric acid with evolution of oxides of nitrogen.

4. The ytterbous ion, Yb^{++}, is green.

URBANA, ILLINOIS

[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

EQUILIBRIA IN THE Fe–H–O SYSTEM. INDIRECT CALCULATION OF THE WATER GAS EQUILIBRIUM CONSTANT

BY P. H. EMMETT AND J. F. SHULTZ

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In a previous paper[1] we have calculated the value of the equilibrium constant for the reaction

$$CO_2 + H_2 = CO + H_2O \qquad K_1 = (P_{CO})(P_{H_2O})/(P_{CO_2})(P_{H_2}) \qquad (1)$$

by combining the equilibrium constants obtained in our experiments[2] on the two reactions

$$Co + H_2O = CoO + H_2 \qquad K_2 = P_{H_2}/P_{H_2O} \qquad (2)$$
$$Co + CO_2 = CoO + CO \qquad K_3 = P_{CO}/P_{CO_2} \qquad (3)$$

The values so calculated were found to be in good agreement with those measured directly by Neumann and Köhler.[3] Such previous calculations made by Eastman and Evans,[4] Eastman[5] and Eastman and Robinson,[6] respectively, had, however, given values about 40% higher than the directly measured equilibrium constants. The first two of these calculations were based on the reactions

$$FeO + H_2 = Fe + H_2O \qquad K_4 = P_{H_2O}/P_{H_2} \qquad (4)$$
$$FeO + CO = Fe + CO_2 \qquad K_5 = P_{CO_2}/P_{CO} \qquad (5)$$
$$Fe_3O_4 + H_2 = H_2O + 3FeO \qquad K_6 = P_{H_2O}/P_{H_2} \qquad (6)$$
$$Fe_3O_4 + CO = 3FeO + CO_2 \qquad K_7 = P_{CO_2}/P_{CO} \qquad (7)$$

The calculations by Eastman and Robinson were made with the help of their own equilibrium data on the reactions

$$SnO_2 + 2H_2 = 2H_2O + Sn \qquad K_8 = P_{H_2O}/P_{H_2} \qquad (8)$$
$$SnO_2 + 2CO = Sn + 2CO_2 \qquad K_9 = P_{CO_2}/P_{CO} \qquad (9)$$

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[1] Emmett and Shultz, THIS JOURNAL, 52, 1782–1793 (1930).

[2] Emmett and Shultz, *ibid.*, 51, 3249–3262 (1929).

[3] Neumann and Kohler, Z. *Elektrochem.*, 34, 218 (1928).

[4] Eastman and Evans, THIS JOURNAL, 46, 888 (1924).

[5] Eastman, Bureau of Mines Information circular 6125 (1929).

[6] Eastman and Robinson, THIS JOURNAL, 50, 1106 (1928).

In view of the importance of knowing the correct values for the water gas equilibrium constant, as well as the values for the equilibria involving iron and its oxides, it seemed worth while to attempt to ascertain whether the above-mentioned discrepancy might be due to errors in previous determinations of the equilibria of Reactions 4, 5, 6 and 7.

Examination of the literature has shown that the equilibrium constants that have been obtained for Reactions 5 and 7 differ considerably among themselves but exhibit no regular variations. The most reliable values agree approximately with those chosen by Eastman.[5] However, values for equilibria involved in Reactions 4 and 6 vary in a somewhat regular manner; they can for the most part be divided into two groups. In Group I are those agreeing with the determinations of Eastman and his co-workers; when combined with equilibrium constants for Equations 5 and 7, they give values for the water gas constant that are 40% or so higher than those directly measured. In the second group are those agreeing approximately with the theoretical curve calculated by combining equilibrium constants of the Fe–C–O system (Equations 5 and 7) and the directly measured value of the constants for Equation 1. A study of the apparatus and procedure employed by these two groups of workers made it seem possible that the values in the first group constitute what might be termed false equilibria in that they may have been influenced by an abnormal consumption of hydrogen by the surface of the iron oxide specimens. Such surface effects had been observed by us during the determination of the equilibrium in Reaction 3. They had also been noted by a number of previous workers.[7]

It seemed that the use of a dynamic rather than a static method would eliminate this source of error. The present paper gives the results of a series of equilibrium measurements obtained by a dynamic method on Reaction 4, at temperatures between 600 and 1000°, and on Reaction 6 at 700 and 800°.

Apparatus and Procedure

The dynamic method used in the present experiments is almost identical with that reported in a previous paper.[1] It consisted essentially in passing steam–hydrogen mixtures over an iron–iron oxide mixture and analyzing the effluent gases for water vapor and for hydrogen. Equilibrium was approached both from the side of reduction and of oxidation.

The apparatus is shown in Fig. 1. It consisted of a saturator, A; a reaction tube, J; an electric furnace, B; and an analytical apparatus, C and D. The saturator consisted of two towers containing glass beads and immersed in a thermostat controllable to ±0.1°. Tank hydrogen, after being freed from oxygen by hot copper, was passed through a flowmeter and mixed with excess steam from a steam boiler; the steam–hydrogen mixture was passed through the thermostated saturator towers.

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[7] Richardson, Vibrans and Bell, Science, 56, 27 (1922); Pease and Cook, THIS JOURNAL, 48, 1199 (1926); Taylor, *Chem. Met.*, 27, 1263 (1922).

The reaction chamber was a silica tube, flanged and ground at one end to fit tightly against a similar flanged and ground pyrex glass tube. The two tubes were drawn together by a brass clamp, padded by asbestos washers and were made gas-tight by a layer of de Khotinsky wax over the joint. The other end of the quartz tube was drawn down and sealed to a small quartz tube in order to decrease the dead space between the oxide mixture and the analytical apparatus. The quartz reaction tube was surrounded by a heavy copper jacket for a distance of about 20 centimeters and packed with 85% magnesia into the electric furnace shown in the diagram. The copper cylinder surrounding the reaction tube fitted tightly into the alundum tube upon which the nichrome heating element was wound. It was centrally located in the furnace, being about 15 centimeters from each end.

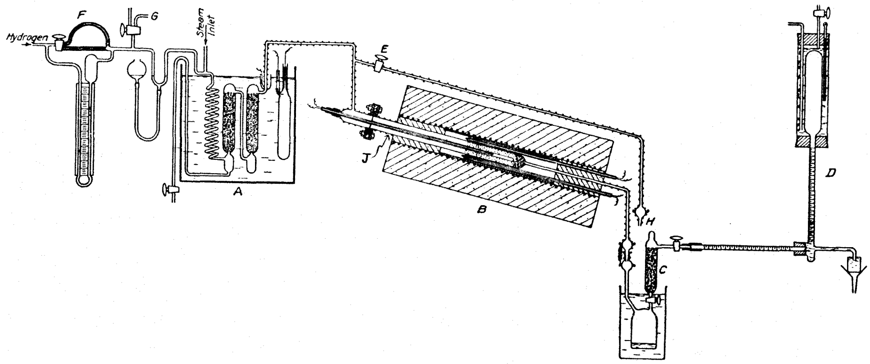

Fig. 1.—Apparatus.

In all of the final runs temperatures were measured by calibrated Pt–Pt-Rh thermocouples in conjunction with a Type K potentiometer. One couple was placed in a thin quartz thermocouple well in the center of the iron–iron oxide mixture, as shown in Fig. 1. The other Pt–Pt-Rh couple was placed in contact with the outside of the reaction tube. During each run it was moved along the tube to obtain the lengthwise temperature gradient. The gradient along the oxide mass was found to agree with that obtained on the outside couple, and was accordingly measured only a few times. The iron–iron oxide mass was about 5° cooler at each end than in the center. The gradient across the reaction tube was usually only one or two degrees; in a few runs it was as much as five degrees.

In the large number of preliminary experiments, alumel–chromel couples calibrated initially at 100 and 444° were used in conjunction with a portable potentiometer for measuring the temperature of 'the reaction tube. Unfortunately, during use the thermocouples became very brittle and broke before a final calibration over the range of temperatures used could be made.

The high reactivity desired in these measurements was obtained by using as a source of iron synthetic ammonia catalysts.[8] Sample A contained 0.5% ZrO_2 and 0.5% Al_2O_3. Sample B was a "pure iron" catalyst containing only 0.15% Al_2O_3.

The analytical apparatus was very similar to that previously described. The gas pipet D was of 250-cc. capacity and was water jacketed in order to eliminate any uncertainty as to its temperature. The weighing tube C was connected to the exit of the reaction vessel by a ground joint. All glass tubing between the thermostat and the reaction tube and at the exit of the reaction vessel was heated electrically to prevent

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[8] Eastman, THIS JOURNAL, 44, 975 (1922).

condensation of any of the moisture present. Dehydrite was used in the weighing tube to catch any moisture not condensed in the main bulb of the tube. The specially designed gas pipet could be attached by a rubber connection directly to the weighing tube and exerted practically no back pressure in the line.

In carrying out the experiments, approximately 54 g. of the fused Fe_3O_4 was placed in the quartz reaction tube. The latter was packed into the furnace and connected as shown in the diagram. The iron oxide was then reduced completely by hydrogen at approximately 600°. At each furnace temperature at which runs were made the saturator was set at such a temperature as to give a steam–hydrogen mixture intermediate in composition between that of Curve I and that of Curve II, Fig. 2. Each run consisted in attaching the analytical apparatus to the exit of the reaction tube and determining the weight of water and volume of hydrogen in the exit gas passed during a given time. The composition of the entering gas was carefully checked at each saturator temperature to make certain that the steam–hydrogen mixture entering the reaction tube corresponded closely to that calculated from the temperature of the saturator. In the course of each experiment the following data were taken: temperature of catalyst, as measured by each of the thermocouples; flowmeter reading; temperature of the flowmeter, of the saturator bath, of the condenser surrounding the weighing tube, and of the gas in the pipet; the time of the run; the apparent volume of hydrogen collected; the height of final water level in the pipet above the water level at its exit; barometric pressure; and weight of water collected in the U-tube. The "U"-tube was always first carefully wiped with alcohol and then weighed to constant weight. From these data

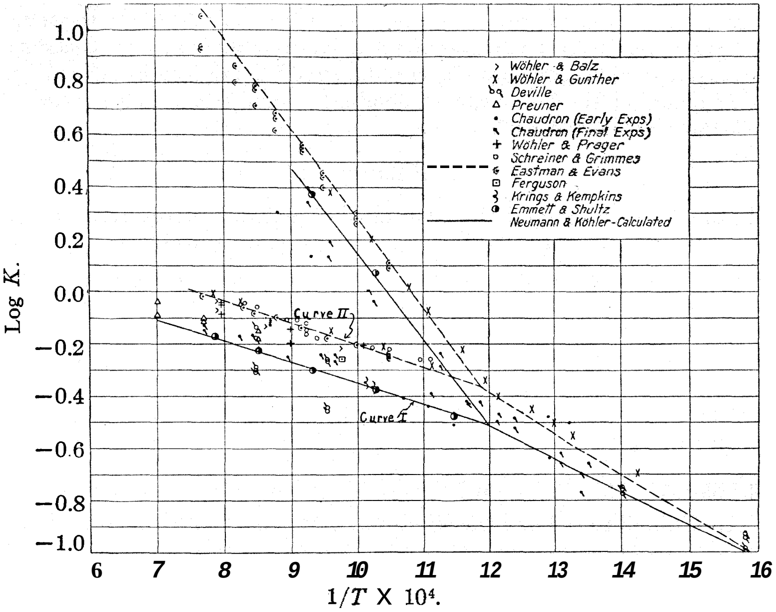

Fig. 2.—Variation with $1/T$ of log K, where $K = (H_2O)/(H_2)$ in equilibrium with FeO–Fe, Fe_3O_4–FeO or Fe_3O_4–Fe. Curve 1 is calculated by combination of the "best values" for the equilibrium constants of the Fe–C–O system and direct water gas constants as measured by Neumann and Kohler. Curve II is the experimental curve of Eastman and Evans.

the exit and entering steam–hydrogen ratios could be calculated. One could also calculate the average composition of the iron–iron oxide mixture in the reaction tube.

When the accumulation of oxide on the iron sample decreased the rate of attainment of equilibrium too greatly, the temperature of the saturator was dropped sufficiently to cause the entering steam–hydrogen ratio to be smaller than that corresponding to **Curve I**, Fig. *2*. Runs were then continued until most of the oxide was removed. Values of K_4 were determined in this way at intervals of 100° from 600° to 1000°, inclusive.

The two series of determinations of equilibria over $FeO–Fe_3O_4$ were carried out after oxidizing the Fe to FeO by long-continued steaming with a steam–hydrogen ratio a little too small to produce Fe_3O_4. This oxidation was continued until the exit steam–hydrogen ratio was identical with the entering, indicating that any iron remaining in the sample was covered effectively by a layer of FeO and would therefore have no influence on measurements of the $FeO–Fe_3O_4$ equilibrium. Equilibrium values were obtained over $FeO–Fe_3O_4$ at **700** and **800°**.

Results

In Table I are averaged the results of a number of preliminary experiments on the Fe–FeO system. The temperatures are those measured by the alumel–chromel couple at the center of the mass of iron–iron oxide.

TABLE I

PRELIMINARY EQUILIBRIUM DATA FOR REACTION 4 IN $H_2O–H_2–Fe–FeO$ SYSTEM

Temp., °C.		**600**	**700**	**800**	**900**	1000
Runs 40–329	$K = H_2O/H_2$	**0.343**	**0.413**	**0.493**	**0.591**	**0.679**
No. of runs averaged		**6**	40	**38**	**19**	**11**

In Tables II, III, IV, V and VI are given the data obtained in the final runs. In Cols. **3** and 4 are the inlet and exit steam–hydrogen ratios corresponding to the temperatures listed in Col. 2. In Col. 5 of each table are the equilibrium values corrected for convenience to 600, 700, 800, 900 and 1000°, respectively. The temperatures recorded in Col. 2 are the averages between the hottest point indicated by the outside couple and the coolest portion of the sample indicated by the inside couple.

TABLE II

EQUILIBRIUM DATA FOR REACTION **4** AT **600°**

Run	Temp., t°C.	Entering H_2O/H_2	Exit H_2O/H_2 $= K_4$ for t°C.	K_4 corrected to 600°C.
350	587	0.51	0.313	0.324
351	589	.51	.306	.315
352	590	.51	.322	.331
353	625	.51	.354	.333
354	621	.51	.350	.332
355	619	.51	.350	.334
376	581	.21	.299	.315
377	622	.21	.361	.342
378	597	.21	.345	.348
379	599	.21	.341	.342
			Average	.332

TABLE III

EQUILIBRIUM DATA FOR REACTION 4 AT 700°

Run	Temp., t°C.	Entering H_2O/H_2	Exit H_2O/H_2 = K_4 for t°C.	K_4 corrected to 700°
345[a]	710	0.21	0.437	0.424
346[a]	706.5	.21	.433	.427
356	706	.51	.428	.423
357	707	.51	.432	.426
358	725	.51	.441	.420
359	715	.51	.437	.424
360	702.5	.21	.420	.418
361	698	.21	.418	.420
362	699	.21	.416	.417
			Average	.422

[a] These values were obtained on Sample B. The other values were all obtained on Sample A.

TABLE IV

EQUILIBRIUM DATA FOR REACTION 4 AT 800°

Run	Temp., t°C.	Entering H_2O/H_2	Exit H_2O/H_2 = K_4 for t°C.	K_4 corrected to 800°
332[a]	807	0.20	0.519	0.513
333[a]	805	.20	.478	.474
334[a]	805	.20	.500	.496
336[a]	795	.20	.498	.503
337[a]	817	.20	.504	.490
365	816	.67	.511	.498
366	818.5	.67	.517	.502
367	817	.67	.514	.500
369	817	.20	.519	.502
370	818	.20	.515	.500
371	814	.20	.504	.509
			Average	.499

[a] These values were obtained on Sample B. The other values were all obtained on Sample A.

TABLE V

EQUILIBRIUM DATA FOR REACTION 4 AT 900°

Run	Temp., t°C.	Entering H_2O/H_2	Exit H_2O/H_2 = K_4 for t°C.	K_4 corrected to 900°
380	899	0.77	0.599	0.600
381	900	.77	.595	.595
382	886	.77	.576	.586
383	917	.77	.623	.610
390	902	.39	.595	.593
391	901	.39	.598	.597
392	899	.39	.590	.591
			Average	.594

In Tables VII and VIII are recorded the few equilibrium values obtained at 700 and 800° for Reaction 6. The temperatures in these runs were measured with the alumel-chromel couples and were accordingly subject to the above-discussed uncertainties.

TABLE VI

EQUILIBRIUM DATA FOR REACTION 4 AT 1000°

Run	Trmp., t°C.	Entering H_2O/H_2	Exit H_2O/H_2 $= K_4$ for t°C.	K_4 corrected to 1000°
384	979	0.91	0.646	0.662
385	986	.91	.656	.667
386	1020	.91	.692	.677
387	1013	.40	.683	.673
388	1014	.40	.683	.672
389	1015	.40	.677	.665
			Average	.669

TABLE VII

APPROXIMATE EQUILIBRIUM DATA FOR REACTION 6 AT 700°

Run	Temp., t°C.	Entering H_2O/H_2	Exit H_2O/H_2 $= K_4$ for t°C.	K_4 corrected to 700°
307	702	0.98	1.176	1.152
308	702	.98	1.288	1.264
309	697	.98	1.110	1.146
319	709	1.35	1.266	1.158
320	705	1.35	1.264	1.200
321	700	1.35	1.166	1.166
			Average	1.181

TABLE VIII

APPROXIMATE EQUILIBRIUM DATA FOR REACTION 6 AT 800°

Run	Temp., t°C.	Entering H_2O/H_2	Exit H_2O/H_2 $= K_4$ for t°C.	K_4 corrected to 800°
310	802.5	0.98	2.462	2.432
314	800	2.64	2.390	2.390
315	800	2.64	2.362	2.362
322	802.5	1.35	2.363	2.333
323	802.5	1.35	2.367	2.337
325	800	2.63	2.350	2.350
326	800	2.63	2.372	2.372
			Average	2.368

In a number of the preliminary experiments the space velocity was lowered. No change in the exit ratio of steam to hydrogen was thereby produced. This constancy in composition of the exit gas at different rates of flow is further evidence that true equilibrium was being attained. All runs listed in Tables II to VI were made with an inlet hydrogen flow of about **23** cc. per minute.

The accuracy of the above equilibrium data depends upon the accuracy with which three measurements were made, the temperature of the iron–iron oxide, the volume of hydrogen passing through the reaction tube during a certain time, and the weight of water vapor passing in the same period of time.

The volume of hydrogen and the weight of water obtained per unit time were measured with considerable accuracy. The measurement of the

250 cc. of hydrogen could not, it seems, involve an uncertainty of more than ±0.5 cc. or 0.2%; this represents the summation of possible errors in reading the pressure, temperature and volume of gas in the pipet. Assuming an uncertainty of ±1 mg. in the weight of water obtained in each run, the total maximum errors that it seems might have been entailed in individual experiments in the analysis of the exit gas would accordingly range from ±1.9% at 600° to ±1.1% at 1000° for the Fe–FeO system, and from ±0.5% at 800° to ±0.7% at 700° in the FeO–Fe_3O_4 system.

In the experiments in which Pt–Pt-Rh thermocouples were used, together with a Type K potentiometer, the uncertainty in the temperature corresponding to a particular equilibrium value should not exceed ±6° at 600 and 700°, ±7° at 800 and 900° and ±9° at 1000°. The temperature at any particular portion of the reaction tube is known more accurately than this. A temperature uncertainty of this amount, however, results from the impossibility of ascertaining precisely which portion of the metal oxide mass determines the measured equilibrium value in a given run. The temperature uncertainty in the two series of runs on the FeO–Fe_3O_4 system, and in the preliminary runs on the Fe–FeO system is harder to estimate. The consistency of the values in the latter runs and their general agreement with those of the final runs would indicate that the temperatures measured with the alumel–chromel couples are probably correct to within ±10°.

When the above-mentioned errors are taken into consideration, the values of K_4 at 600, 700, 800, 900 and 1000" are 0.332, 0.422, 0.499, 0.594 and 0.669, respectively, each value being correct to ±0.012 unit. The values of K_6 at 700 and 800° are approximately 1.18 and 2.37, respectively. The above errors are estimated maximum errors that might exist in any one experiment. The probable errors calculated from the above data are of course very much smaller.

It will be noted in the above data that there is no difference between the values obtained with iron oxide, Sample A, and those obtained with Sample B. This observation was also apparent in the runs summarized in Table I. This indicates that the small content of Al_2O_3 or ZrO_2 does not materially affect the free energy of the iron samples.

In the above experiments the oxygen content of the samples was varied over wide limits with no influence on the equilibrium constant obtained. At one point equilibrium values taken from the high steam–hydrogen side remained constant, while the percentage of oxygen in the iron sample increased steadily from about 0.4 to about 5%. The first two runs after freshly oxidizing or reducing the sample were omitted in the above averages in order to exclude any possible surface effect from the final equilibrium values.

Discussion of Results

Logarithms of the values of K_4 and K_6 observed by various workers are plotted against $1/T$ in Fig. 2. Curve I was calculated by combining the "best values" chosen by Eastman[8] for the equilibria in Reactions 5 and 7 with the directly measured values of the water gas equilibrium of Reaction 1 as measured by Neumann and Köhler.[3] Curve II is one drawn by Eastman and Evans as being representative of their own values for the equilibria of Reactions 4 and 6. It is to be observed that the results of Eastman and Evans, of Schreiner and Grimmes[9] and of Wohler and Günther[10] agree fairly well with each other and with Curve II, but are about 40% higher than values lying along Curve I. The results of Van Groningen are said to be in agreement with these workers too, though his dissertation has not been available to us. The results of Wohler and Prager,[11] Wohler and Balz,[12] Chaudron,[13] Deville[14] and Preuner[15] lie, for the most part, between the two curves. The values obtained by the last three workers agree more closely with Curve I than with Curve II, though they are somewhat erratic. Finally, it will be noted, the values obtained in the present experiments are in excellent agreement with Curve I and are consistent with the maximum values of K_4 fixed by the experiments of Krings and Kempkens[16] and of Ferguson.[17]

Because of the importance of knowing the correct values for the equilibria of Reactions 4 and 6 and of gas–solid equilibria in general, it has seemed worth while to examine carefully the procedure and apparatus employed by the various above-mentioned workers with a view of ascertaining a possible cause of the large discrepancies that exist in the present equilibrium data.

The errors that may exist in the experimental determination of the equilibrium constant are of two kinds: (1) those resulting from incorrect observation of the temperature during a run, or faulty measurement of the partial pressure of water vapor or of hydrogen in the gaseous mixture at the end of an experiment; (2) those due to failure to obtain true equilibrium between the steam–hydrogen mixture and the solid phases indicated in Equations 4 and 6.

It seems very unlikely that the first type of error could be the entire cause of the above-mentioned discrepancies. In most cases the tempera-

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[9] Schreiner and Grimmes, *Z. anorg. Chem.*, 110, 311 (1920).

[10] Wohler and Günther, *Z. Elektrochem.*, *29*, *276* (1923).

[11] Wohler and Prager, *ibid.*, 23, 199 (1917).

[12] Wohler and Balz, ibid., 27, 406 (1921).

[13] Chaudron, *Compt. rend.*, *159*, *237* (1914); *Ann. chim. phys.*, 16, 221 (1921).

[14] Deville, *Compt. rend.*, 70, 1105, 1210 (1870); 71, 30 (1871).

[15] Preuner, *Z. physik. Chem.*, 47, *385* (1904).

[16] Krings and Kempkens, *Z. anorg. allgem. Chem.*, 183, 225 (1929).

[17] Ferguson, *J. Wash. Acad. Sci.*, 13, 275 (1923).

ture of the sample was probably known with reasonable accuracy. The partial pressure of water could be in error only to the extent that there was any inaccuracy in measuring the temperature of the water in the thermostated bulb attached to the reaction tube in static experiments, or inaccuracy in determining the weight of water passing the iron samples per unit time in the experiments made by a dynamic method. No large uncertainties seem to have existed in either of these measurements. The principal error in measuring the partial pressure of hydrogen in static experiments arises from possible evolution of inert gas from the walls of the reaction tube of the metal sample during a run, or from possible leaking of air into the apparatus. Either occurrence would cause the total pressure and hence the apparent partial pressure of hydrogen to be too high; this would lower the apparent value of the equilibrium ratio of steam to hydrogen. Although this might explain some of the discrepancies between the various static experiments, it could not possibly account for the results of some of the static experiments being 40% higher than those obtained by the present dynamic method.

It has seemed to us that the cause of the discrepancy is of the second type. A careful consideration of the experiments of the various principal workers makes it appear probable that in the experiments performed by the static Deville method a false equilibrium has been measured—an equilibrium that differs from true equilibrium because of an abnormal consumption of hydrogen by a "surface oxide" present to a greater or less extent in all the static experiments carried out. Before discussing the work of the various authors it will be well to define what is meant by the "surface effect" here referred to.

Several instances are recorded in the literature in which the passage of a steam–hydrogen mixture over a freshly oxidized metal has resulted for a brief period in an exit steam–hydrogen ratio much higher than that corresponding to equilibrium with the massive metal–metal oxide phases. Conversely, passage of a steam–hydrogen mixture over freshly reduced metal surfaces has resulted in such an evolution of hydrogen that the effluent gas has for a short time possessed much less steam than corresponded to the normal equilibrium. Thus, Richardson, Vibrans and Bell noted the evolution of hydrogen in excess of equilibrium requirements when they passed steam over iron freshly reduced from iron oxide. Almquist and Black[18] and Emmett and Brunauer[19] have observed the definite formation of oxide on iron synthetic ammonia catalysts by ratios of steam to hydrogen much below equilibrium. Pease and Cook[7] noted excessive hydrogen evolution on passing steam over finely divided nickel and excessive hydrogen consumption in passing steam–hydrogen mixtures over

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[18] Almquist and Black, THIS JOURNAL, 48, 2814 (1926).

[19] Emmett and Brunauer, *ibid.*, 52, 2682 (1930).

freshly formed nickel oxide. The present authors[1] have called attention to similar phenomena in their study of the equilibria in Reactions 2 and 3. The effect is particularly observable in this latter system. In Fig. 3 is reproduced a diagram taken from the last mentioned paper. It clearly shows the manner in which such an effect can raise the ratio of CO_2/CO to a value much in excess of equilibrium if the surface of the oxide concerned is completely oxidized. The oxidation of the surface metal atoms by a gaseous oxidizing agent or reduction of the surface atoms of a metal oxide by a reducing gas thus appears to proceed with a greater decrease in free energy than does the oxidation of the massive metal to oxide or reduction of the normal oxide to massive metal. There are at present no data defining precisely the thickness of the "surface" to which such abnormal phenomena are restricted. All quantitative evidence available is, however, consistent with this "surface effect," being limited for the most part to the few outer layers of atoms of the metal or oxide.

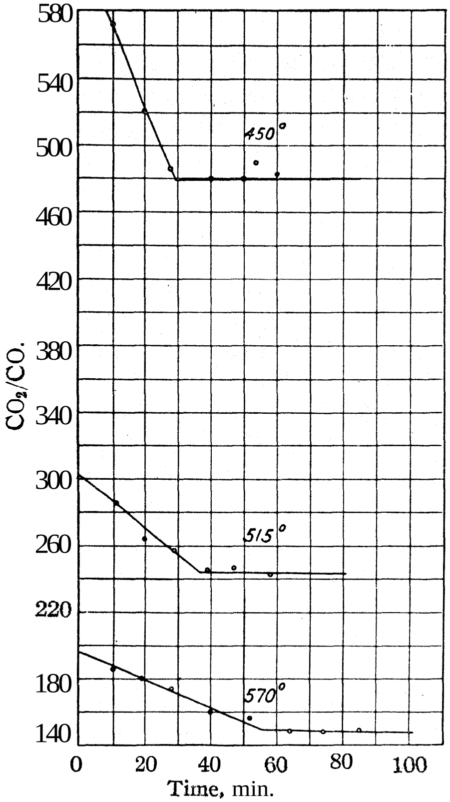

Fig. 3.—Typical curves showing the effect of surface oxide on the CO_2–CO equilibrium value over a cobalt–cobalt oxide mixture. The three series of runs shown were taken immediately after oxidation of the cobalt surface to CoO. The entering CO_2–CO ratios in the 570, 515 and 450° runs shown were 102, 194 and 324, respectively.

When the experiments of different workers are considered from the standpoint of the above-described surface effect, some interesting correlations appear.

Eastman and Evans, Schreiner and Grimmes, and Wohler and Günther used almost identical apparatus and procedure, and obtained values that are in good agreement with each other but are, in general, some 40% higher than those corresponding to Curve I in Fig. 2. The method used consisted in permitting water vapor from a thermostated water bulb to come in contact with samples of finely divided iron or iron oxide held in a quartz tube at some definite temperature. Equilibrium was said to have been reached when the total pressure indicated on an attached manometer became constant. These workers approached equilibrium from the reduction side by then merely increasing the temperature 25 or 50° after having obtained equilibrium from the oxidation side, and permitting the initially low steam–hydrogen ratio to adjust itself to the higher temperature. The samples of iron used were completely reduced in hydrogen initially and introduced into the quartz reaction tube as metallic iron. Evacuation of the apparatus was then carried out with the iron sample heated to free the apparatus from inert gases and decrease the pressure to that of the water vapor from the thermostated water bulb. In some of the experiments in which it was desirable to use a sample of known oxygen content, the iron samples were partially oxidized by continued evacuation until they were converted partially to oxide. In none of the experiments of these three authors was any mention made of approaching equilibrium from the reduction side by adding a large excess of hydrogen.

From this brief description of the procedure followed by these workers it will be apparent that at the start of every experiment mentioned by them iron samples had already been subjected to considerable exposure to steam. Hence each particle of iron must have been oxidized to some depth before the beginning of an experiment. Furthermore, in these experiments the final volume of hydrogen at equilibrium was of the order of only 2 or 3 cc. (S. T. P.) according to calculations based upon the internal volume of the apparatus and the final pressure of hydrogen present. It would seem, accordingly, that conditions were in each instance favorable for the operation of the "surface effect" mentioned above. The small volume of hydrogen in contact with a completely oxidized iron oxide surface would, in accordance with all of the above-mentioned instances, be expected to be partially consumed, thus resulting in a steam–hydrogen ratio much in excess of the true equilibrium value. The method used in approaching equilibrium from the hydrogen side would merely shift this surface effect to another temperature but still leave conditions suitable for it to be operative.

In marked contrast to the above-mentioned work is that of Deville, of Chaudron and of Preuner. They, in general, used a static apparatus similar to that of the first group of workers. However, the procedure employed was such as to eliminate partially the above-mentioned surface effect in at least some of their experiments. Deville and Preuner actually added excess hydrogen to the apparatus and observed the equilibrium resulting from the reduction of an iron oxide sample. Chaudron, in changing from the system $FeO–Fe_3O_4$ to the system Fe–FeO added excess hydrogen to the apparatus and after reduction evacuated it with the sample of iron cold. Any runs made immediately after such reduction without intervening evacuation with the sample hot should likewise not have been subject to a marked surface effect. Insufficient description of the exact procedure used by these three workers is given, however, to permit one to conclude definitely whether all of the discrepancy between this second group of workers and the first group is due to the influence of the surface effect, or is due in part to errors of Type 1.

Several interesting observations may be made in regard to the work of Deville and of Preuner.

Deville originated the static apparatus subsequently used by most workers in metal–metal oxidesteam–hydrogen equilibrium measurements. He obtained values at only two temperatures in the range covered by our own experiments, namely 907 and 767°, the boiling points of zinc and cadmium. His results at these temperatures are shown in Fig. 2. At 767° it will be noted that the four equilibrium values obtained by Deville fall distinctly into two groups. The two upper values obtained from the oxidation and reduction sides with the water-bath temperature at 15 and 15.4°, respectively, are in perfect agreement with each other, but differ greatly from two lower values obtained with the water-bath supposedly at 0°. No temperature measurements were made of the water in the inner bulb in the experiments of Deville, the temperature being assumed to be that of the surrounding water-bath. It is interesting to note that the four values at 767° are brought into perfect agreement by assuming that the water in the bulb attached to the reaction tube was at 4° instead of 0°. Since at 4° water has its maximum density, it does not seem improbable that in his experiments the water bulb was located at the bottom of an unstirred ice-bath where the temperature might easily have been 4°. Similarly at 907° the three low values were obtained with the water bulb immersed in an ice-bath, whereas the two upper values were obtained with the temperature of the water-bath at 15°. In this case, however, an assumed temperature of about 3° would be necessary to bring the two groups of results into agreement. It seems highly probable that this error in the temperature of the water-bath in the runs at 767 and 907° may have caused the discrepancies in his own experiments at these temperatures.

Preuner, working with a Deville type apparatus at temperatures of 900, 1025 and 1150°, obtained equilibrium values for Reaction 4. He, like Deville, took precautions to approach the equilibrium from the reduction side by actually introducing an excess of hydrogen and observing the pressure decrease. In Fig. 2 the higher of the values obtained by Preuner at each temperature are those in which equilibrium was approached from the high steam–hydrogen side. Those obtained from the reduction side are on an average only 5 to 10% above Curve I.

One observation not previously mentioned in connection with Preuner's work seems important. Figure 4 is a reproduction of Figure 24 of Preuner's paper. In his article in connection with this figure an experiment is described in which he merely wished to demonstrate the slowness with which a small amount of iron oxide would react with hydrogen at 900°. Water vapor at a pressure of 46.6 mm. was permitted to react in his static apparatus with a sample of completely reduced iron until the pressure had built up to 115 mm. A sufficient amount of hydrogen was then admitted to build up the pressure in the apparatus to about 130 mm. The pressure quickly dropped to an apparently constant value of about 125 mm. Preuner did not include this value in his equilibrium data, believing apparently that true equilibrium had not been attained. This is the only experiment in which after reaching equilibrium from the oxidation side he introduced hydrogen into the apparatus without further evacuation and resulting oxidation of the sample. As shown in Fig. 2, the equilibrium constant that we have computed from this one experiment agrees well with Curve I. It seems to be added evidence in favor of the validity of Curve I values and is apparently one static experiment in which the above-mentioned surface effect was entirely eliminated.

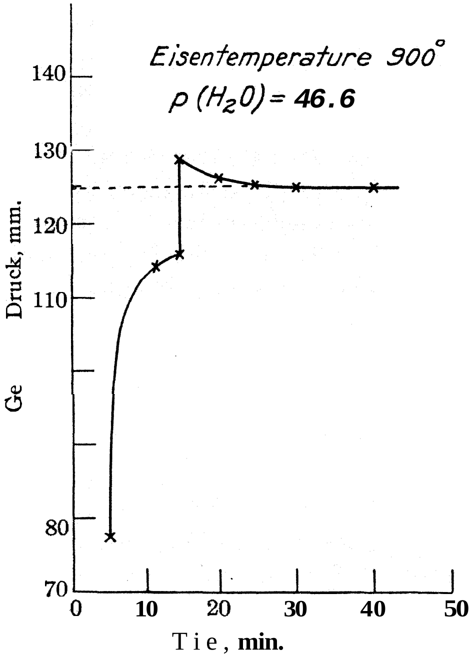

Fig. 4.—Variation with time of the P_{H_2O}/P_{H_2} over a sample of completely reduced iron in a static experiment by Preuner. The experiment is unique among all recorded static experiments on the Fe–H–O system in that after permitting the initially low steam–hydrogen ratio to increase nearly to equilibrium, an excess of hydrogen was added without intervening evacuation. The final steady state pressure shown in this figure corresponds to a value for K_4 in agreement with those of Curve I, Fig. 2.

The values obtained by Wöhler and Prager and by Wöhler and Balz agree much more closely with Curve II, Fig. 2, than with Curve I. The values obtained from the oxidation side are susceptible to the above-mentioned surface effect since evacuation of the reaction vessel and hot sample with its attendant oxidation of the surface of the iron was carried out before each run. However, equilibrium was approached from the reduction side by admitting an excess of hydrogen—"sometimes as much as 120 cc."—to an oxidized sample and permitting the pressure to decrease to a constant value. It is not clear why these latter equilibrium values should fail to agree more closely with Curve I.

Any surface effect occurring in a dynamic system is quickly eliminated by the large amount of steam and hydrogen passing through the reaction tube. Consequently, the equilibrium measurements reported in the present paper should be free from this error. They constitute the first measurements made upon Reaction 4 by a flow system in which the point of equilibrium was determined by analysis of the effluent gas from the reaction tube. The excellent agreement of the experimental points among themselves and with Curve I attests to their probable correctness.

The experiments of Krings and Kempkens and of Ferguson were also made by a flow method. They differ from our own experiments, however, in that the value of the equilibrium constant is deduced from the variation in composition of the iron or iron oxide samples when treated for a number of hours with a given steam–hydrogen mixture. The results of Krings and Kempkens shown in Fig. 2 represent ratios of steam to hydrogen that sufficed to form an appreciable amount of oxide on the iron samples used. Their measurements fix the upper limits to the values of K_4 at the temperatures used. Similar experiments performed with slightly lower steam–hydrogen ratios and with iron oxide as a starting material would fix the lower limit for K_4. Ferguson's measurements unfortunately were made upon a sample of pure electrolytic iron that had been heated in hydrogen for many hours at 900 to 1000°, and that was therefore doubtless extremely inactive and slow to oxidize. At 750°, after six hours exposure of the Samples of the iron to streaming mixtures of steam and hydrogen in which the ratios of steam to hydrogen were 0.476, 0.540, 0.568 and 0.595, respectively, the final samples analyzed 99.98, 99.9, 98.0 and 93.6% iron. These experiments of Ferguson definitely indicate that the value for the equilibrium constant for the conversion of Fe into FeO is not greater than 0.568 at 750°, assuming that the 2% oxygen content of this final sample is not present as solid solution. They cannot be considered, however, to contribute information as to the exact value of the equilibrium constant.

It is of course true that the surface effect mentioned and described above can be supposed to affect the equilibrium value only in case the duration of each experiment is insufficient to permit the true equilibrium value characteristic of the mass of iron–iron oxide to be attained. The slowness with which the establishment of true equilibrium throughout the mass of Fe–FeO takes place is evidenced by the fact that, according to the recent work of Krings and Kempkens, when a gas stream containing such a moisture content as to make its steam–hydrogen ratio slightly less than the equilibrium value for Reaction 4 above is passed over a sample of Fe_2O_3, complete reduction at 715° is not obtained for a great many hours. Thus, at the end of eight hundred hours, about 0.6% of oxygen still remained in such a sample.

Eastman and Evans observed that the equilibrium ratio of steam to hydrogen over an iron–iron oxide mixture at 775° decreased rapidly as the oxygen content of the solid phase fell below 5%. They interpreted this as being an indication that as much as 5% oxygen would dissolve in a sample of iron. However, Krings and Kempkens have recently determined the solubility of oxygen in iron and found it to be of the order of 0.1% or less. Possibly the decrease in the steam–hydrogen ratios in the experiments of Eastman and Evans at these low oxygen contents was the result of enough iron being exposed in the initial sample to eliminate partially the surface error outlined above and to cause the values for the equilibrium steam–hydrogen ratio to deviate more and more toward true equilibrium as the percentage of oxygen in the solid phase decreased.

The correlations mentioned in the above discussion are, we believe, significant and must somehow be explained. The tentative explanation here proposed, involving what has been termed "surface effect," seems consistent with most of the known experimental data. However, it cannot be accepted as final until conclusively demonstrated in a series of static experiments in which the exact technique necessary to produce the true equilibrium has been studied in detail. To this end additional experimental work is being undertaken at this Laboratory. An attempt will be made to prove the possibility of obtaining either false equilibrium values or true equilibrium values in a given static apparatus by merely changing one's procedure slightly. Further details as to the nature of this surface effect will accordingly be deferred to a later paper. At that time equilibrium data for steam–hydrogen over Fe–Fe_3O_4 and additional data for the FeO–Fe_3O_4 system will also be presented.

The Equilibrium Constant for the Water Gas Reaction

The value for the equilibrium constant for Reaction 1 can be calculated readily by combining equilibrium data for the Fe–C–O system of Equation 5 with the values of K_4 obtained in the present experiments. Such a calculation gives water gas constants agreeing with the directly measured values of Neumann and Kohler as closely as do the experimental values determined in the present paper agree with Curve I of Fig. 2. This calculation assumes the accuracy of the data for the Fe–C–O system. In Fig. 5 are shown the data for the Fe–C–O system. Curve I represents the "best values" as chosen by Eastman in his first paper.[8] The recent experimental values of Schenck and his co-workers[20] are also included. Curve II, Fig. 5, represents Eastman's[8] latest choice of the "best values" for this system.

In Table IX are summarized the values for the water gas equilibrium constants obtained in different ways. Columns 2 and 3 contain those obtained by the direct measurement of Hahn[21] and of Neumann and Kohler,

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[20] Schenck, *Stahl Eisen*, 46, 665 (1926); *Z. Elektrochem.*, 34, 399 (1928); *Z. anorg. Chem.*, 167, 315 (1927); 167, 254 (1927); Schenck and Dingmann, *ibid.*, 166, 113 (1927); 171, 239 (1928).

[21] Kahn, *Z. physik. Chem.*, 44, 5131 (1903); 48,735 (1904).

respectively. The values of the water gas equilibrium constant of Reaction 1 calculated by use of the steam–hydrogen and CO_2–CO equilibria with Co–CoO mixtures are shown in Col. 4. Those in Col. 5 were obtained by dividing the value of K_4 from our own Fe–H_2O–H_2–FeO equilibrium data, by K_5 as reported by Eastman. Column 6 contains the indirect calculation of Eastman and Robinson based upon their data for Reactions 8 and 9. This is the one remaining indirect calculation giving values for the water gas equilibrium constant that disagree with the directly measured values. The values in Cols. 3, 4 and 5 agree excellently with each other and we believe correspond to the true values of the water gas equilibrium constant over the range of temperature covered.

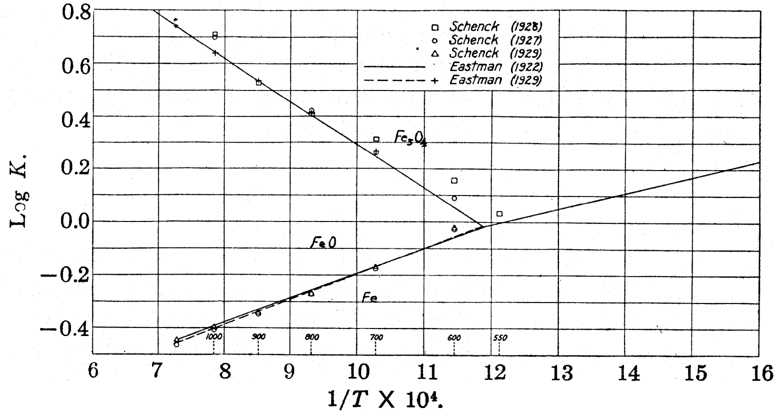

Fig. 5.—Variation with $1/T$ of log K, where K = $(CO_2)/(CO)$ in equilibrium with FeO–Fe, Fe_3O_4–FeO or Fe_3O_4–Fe.

TABLE IX

WATER GAS EQUILIBRIUM CONSTANTS

	Direct measurements			Calculated from	
Temp., t°C.	Hahn	Neumann and Köhler	Co–CoO system	Fe–FeO system	Sn–SnO_2 system
350		0.041			
400		.080			
450		.140	0.137		
500		.200	.207		
550		.290	.297		
600		.410		0.380	
650		.50			0.707
700	0.610	.63		.624	0.882
750	.755	.78			1.078
800	.906	.93		.917	1.294
850	1.071	1.09			
900	1.240	1.29		1.306	
950	1.420	1.44			
1000	1.606	1.66		1.693	

Summary

1. The value of the equilibrium constant $K_4 = P_{H_2O}/P_{H_2}$ for the reaction $FeO + H_2 = Fe + H_2O$ has been determined by a flow method at 600, 700, 800, 900 and 1000" to be 0.332, 0.422, 0.499, 0.594 and 0.669, respectively.

2. The value of the equilibrium constant $K_6 = P_{H_2O}/P_{H_2}$ for the reaction $Fe_3O_4 + H_2 = 3FeO + H_2O$ has been determined by a flow method at 700 and 800° to be 1.18 and 2.37, respectively.

3. Combination of these values with the "best values" of Eastman for the Fe–C–O system gives values for the water gas equilibrium in good agreement with the water gas values determined directly by Neurnann and Kohler.

4. The so-called "surface effect" is presented as a probable reason for the discrepancies between the water gas values as obtained indirectly by other workers and the directly determined values.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE UNIVERSITY OF NORTH CAROLINA]

A STUDY OF THE QUANTITATIVE PRECIPITATION OF CALCIUM OXALATE IN THE PRESENCE OF THE ARSENATE ION

BY J. T. DOBBINS AND W. M. MEBANE

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A study of the quantitative precipitation of calcium oxalate in the presence of the phosphate ion by Dobbins and Mebane[1] showed that the calcium ion could be quantitatively precipitated from a solution containing an excess of phosphate ions. Since the usual method of estimating calcium in calcium arsenate involves the same difficulties met in the phosphate analysis, a similar study was made of the quantitative precipitation of calcium in the presence of the arsenate ion. As the phosphate ion and the arsenate ion are chemically similar, the same method of study was used.

The study was based on the assumption' that the so-called tertiary calcium arsenate, which forms on the addition of ammonium hydroxide to the solution, having a much greater solubility product than calcium oxalate would go into solution and thus the calcium oxalate form. Consequently, if the solution be allowed to stand long enough for this metathesis to be complete, it should be possible to precipitate calcium oxalate in the presence of the arsenate ion. In order to determine the most favorable conditions under which to carry out the precipitation, several series of analyses were made to determine the time required for complete

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[1] Dobbins and Mebane, THIS JOURNAL, 52, 1469 (1930).

transformation of calcium arsenate to calcium oxalate and the effect of temperature and alkalinity of solution at time of precipitation.

After first having found the minimum time necessary for the complete precipitation, determinations were made to determine the difference in results, if any, caused by adding the precipitating agent before and after the solutions were made alkaline with ammonium hydroxide and by varying the alkalinity of solution at time of precipitation. These series were run at 30 and 100°. An excessive amount of ammonium hydroxide, when added first to the solution, appeared to hinder the formation of calcium oxalate. Consequently two series were made using a slight excess of ammonia in one case and 10-cc. excess of concentrated ammonium hydroxide solution in the other, in order to determine the effect of the concentration of ammonium hydroxide on the solution.

Procedure.—A 0.1 N solution of calcium chloride was prepared by dissolving a weighed quantity of Iceland spar in hydrochloric acid. Approximately 0.1 N solutions of disodium arsenate and potassium permanganate were made. As the precipitating agent, a saturated solution of ammonium oxalate was used.

Twenty cc. of the standard solution was taken for each analysis. To this solution 25 cc. of the disodium arsenate was added to give an excess of arsenate ions, and then an excess of ammonium oxalate. The total volume of solution at this point was 80–100 cc. The precipitates were filtered, washed by decantation with distilled water containing a small amount of ammonium hydroxide and transferred on the filter paper to the precipitation beaker. The precipitates were dissolved in dilute sulfuric acid, the solution was brought almost to boiling temperature, and titrated rapidly with the 0.1 N permanganate solution in the usual way. As the precipitate was very finely divided, an inferior grade of filter paper could not be used in this determination. It was found that as accurate results were obtained by titrating the precipitate first formed as by following the usual procedure of dissolving and reprecipitating the calcium oxalate. The losses involved in redissolving the precipitate were as great as the error caused by the adsorption of ammonium oxalate by the precipitate.

TABLE I

EFFECT OF TIME OF STANDING

Twenty cc. of $N/10$ calcium solution used in all cases, made alkaline with ammonia before addition of oxalate

Time, hours	30° $N/10$ $KMnO_4$, cc.	100° $N/10$ $KMnO_4$, cc.
0.25	20.10	20.00
0.5	19.95	20.00
1	20.10	19.95
1.5	20.10	20.00
2	20.10	20.00

TABLE II

EFFECT OF TEMPERATURE. CONCENTRATION OF AMMONIA AND ORDER OF ADDITION OF REAGENTS

Ammonium hydroxide added to the solution before ammonium oxalate. One hour allowed for reaction

30°		100°	
Slight excess NH_4OH $N/10$ $KMnO_4$, cc.	10 cc excess NH_4OH $N/10$ $KMnO_4$, cc.	Slight excess NH_4OH $N/10$ $KMnO_4$, cc.	10 cc. excess NH_4OH $N/10$ $KMnO_4$, cc.
20.60	21.90	20.00	20.10
20.20	20.30	20.05	20.10
20.20	19.95	20.00	20.15
Twenty-four hours allowed for reaction			
20.00	20.05	20.05	20.00
20.00	19.95	20.00	19.95
20.00	20.00	19.95	20.00
Ammonium hydroxide added to the solution after ammonium oxalate. One hour allowed for reaction			
20.00	20.95	20.00	20.30
20.15	19.85	20.00	20.20
19.80	20.10	20.00	20.35
Twenty-four hours allowed for reaction			
19.95	19.95	19.95	20.00
20.00	19.95	19.95	20.00
20.00	20.00	20.00	20.00

Discussion

The formation of calcium oxalate in the presence of the arsenate ion was not as rapid as in the presence of the phosphate ion. Especially was this true at low temperature. Judging from other reactions of arsenates and phosphates, this was to be expected. Due possibly to adsorption of ammonium oxalate by calcium arsenate, the results of the titration were apt to be high if insufficient time were allowed for complete transformation of the calcium arsenate into calcium oxalate. This was also shown by the fact that good results were obtained in all cases where the precipitates were allowed to stand twenty-four hours before filtration or had been formed in solutions only faintly alkaline with ammonium hydroxide and digested at the boiling temperature for one hour. This heating seemed to destroy the flocculent nature of the previously precipitated calcium arsenate and made filtration very difficult, but good results were obtained by this method. The time of addition of ammonium hydroxide made no material difference in the analysis where the higher temperature was used. A large excess of ammonia gave high results in most of the analyses which were allowed to stand for an hour. This is possibly explained upon the difference in the adsorptive power of calcium arsenate which was formed in high concentrations of ammonium hydroxide and that which was formed in solutions only faintly alkaline. Those precipitates which were allowed to stand over for a twenty-four hour period gave uniformly good results. This was due to the complete transformation of the arsenate into the oxalate during this period of standing.

Recommended Procedure

Accurate results were obtained from the following procedure. The solution was made alkaline with ammonium hydroxide and a few drops excess added. After the addition of an excess of ammonium oxalate to the boiling solution, it was kept at incipient boiling temperature and occasionally stirred for ten minutes. After standing for an hour the precipitate was filtered off, washed with distilled water containing a small amount of ammonium hydroxide, transferred on the paper to the precipitation beaker, dissolved in 30 cc. of dilute sulfuric acid, diluted to 100 cc. and titrated rapidly with a 0.10 N potassium permanganate solution.

Summary

1. Calcium oxalate may be precipitated quantitatively in the presence of the arsenate ion.

2. The solution may be made alkaline either before or after the addition of ammonium oxalate, and a small excess of ammonium hydroxide added.

3. The best temperature for precipitation is 90–100°.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 268]

THE PHOTOCHEMICAL FORMATION OF CHLORINE DIOXIDE FROM CHLORINE MONOXIDE IN CARBON TETRACHLORIDE SOLUTION

BY ROSCOE G. DICKINSON AND CECIL E. P. JEFFREYS

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That chlorine monoxide, Cl_2O, is sensitive toward light has long been recognized. In recent years several quantitative investigations of the photochemistry of this compound have been undertaken. Bowen[1] studied the effect of light in the region 4100–4700 Å. on carbon tetrachloride solutions of chlorine monoxide; apparently on the assumption that the products of the reaction were simply chlorine and oxygen, he found from 0.81 to 1.02 molecules of the monoxide decomposed per quantum absorbed. He later measured[2] the effect of light on gaseous chlorine monoxide and concluded that in the gaseous state apparently two molecules of monoxide were decomposed for each quantum of blue and violet light absorbed.

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[1] E. J. Bowen, *J. Chem. Soc.*, 123, 1199 (1923).

[2] Bowen, *ibid.*, 123, 2330 (1923).

The gaseous reaction was studied more extensively by Bodenstein and Kistiakowsky.[3] They concluded that two molecules of monoxide were decomposed per quantum absorbed irrespective of whether the light absorber was chlorine monoxide or added chlorine. They found further that the decomposition was accompanied by the formation of chlorine dioxide; this was shown by the fact that gaseous monoxide developed, on illumination, the absorption bands of the dioxide in the blue and violet. They believed, however, that the quantity of dioxide formed was very small, and they apparently did not regard its formation and presence as any important complicating circumstance in the measurement of the quantum yields.

The mechanism of the decomposition of chlorine monoxide (without reference to ClO_2 formation) has been discussed by Schumacher and Wagner.[4] They have shown that for 4350 Å. the absorption process may be either $Cl_2O + h\nu \longrightarrow Cl_2 + O$ or $Cl_2O + h\nu \longrightarrow ClO + Cl$, and regard the latter as more probable. The character of the absorption spectrum of gaseous Cl_2O[5] indicates that this wave length is energetically capable of producing either of at least two different dissociations.

In the present paper is described an examination of the reaction in carbon tetrachloride solution. It is found that chlorine dioxide is formed on illumination of the solution and that the amount formed is by no means negligible compared with the amount of monoxide decomposed. Moreover, the comparatively high light absorption coefficients of the dioxide make the presence of even small amounts of this compound a disturbing factor in the measurement of the quantum yield of the monoxide decomposition.

The Materials

Carbon Tetrachloride.—Some difficulty was experienced in preparing sufficiently good carbon tetrachloride. The starting point was commercial C. P. material; since this showed some photochemical reaction with chlorine, it was subjected to the following treatment.[6] The liquid was boiled for nine hours in an all-glass reflux apparatus, chlorine being bubbled through continuously. The chlorine was boiled off and the liquid treated with anhydrous sodium carbonate, and distilled twice from an all-glass still with a fractionating column. A middle fraction was used. This product was still found to develop acidity when chlorine was dissolved in it and the solution illuminated for four hours with the blue light source described below. (The acidity was detected by pouring the illuminated chlorine solution into an excess of potassium iodide, titrating to an end-point with thiosulfate and then adding iodate.) Finally some of this carbon tetrachloride which had been refluxed with chlorine was saturated with chlorine dioxide; after standing for several days it was again washed and fractionated. This product developed no acidity on four hours' illumination with chlorine and was used in the experiments described below.

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[3] M. Bodenstein and G. Kistiakowsky, Z. *physik. Chem.*, *116, 371* (1925).

[4] H. J. Schumacher and C. Wagner, *ibid.*, **5B**, 199 (1929).

[5] C. F. Goodeve and J. I. Wallace, *Trans. Faraday Soc.*, 26,254 (1930).

[6] H. Grüss, *Z. Elektrochem.*, 29, *144* (1923).

Chlorine Monoxide.—The chlorine monoxide was prepared in carbon tetrachloride solution by adding an excess of mercuric oxide to carbon tetrachloride about half saturated with chlorine at room temperature. The oxide reacted quickly to give the brownish chlorine monoxide solution. The solid material was filtered off using asbestos in a Gooch crucible. Occasionally the preparations showed a small amount of free chlorine on analysis.

The mercuric oxide used in this preparation was obtained by adding a 50% solution of potassium hydroxide to a saturated solution of mercuric chloride at room temperature. The precipitated mercuric oxide was washed and then dried for two days or more at 120°.

Chlorine.—For the preparation of chlorine monoxide or for absorption measurements chlorine from hydrochloric acid and manganese dioxide, or from a tank, was purified by passing through a train of washing bottles with all-glass connections. The first two bottles contained potassium permanganate solution, the third concentrated sulfuric acid and a fourth glass wool to retain mist. Fresh materials were placed in the train before each experiment. The gas from the train was passed into carbon tetrachloride in a glass stoppered flask.

Chlorine Dioxide.—This was prepared according to the method of Bray.? Eight grams of potassium chlorate and **30** g. of oxalic acid were intimately mixed and moistened with 4 cc. of water in a flask with a side arm. The mouth of the flask was sealed and the mixture heated to 60°. The evolved gas was passed into carbon tetrachloride.

The Apparatus.—The arrangements for illuminating the solution and measuring its transmission are shown in plan in Fig. 1. Light from the quartz mercury arc A operated from a d. c. generator with a voltage regulator, passed, when the shutter B was opened, through a hole 1 cm. in diameter in a removable cap, C. It then passed through the filter box D through which water was flowed. The light filters E were submerged in this box. The light was then collimated by the lenses F.

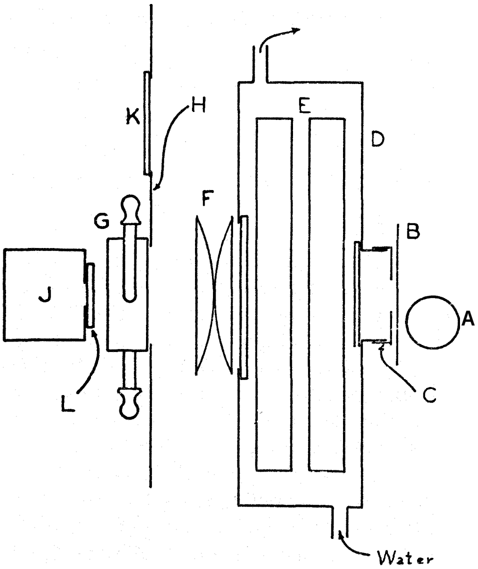

Fig. 1.—Plan view of photochemical apparatus.

The pyrex glass reaction cell G was 1.06 cm. thick internally with flat faces **3** cm. in diameter. The volume of solution which it held was 6.9 cc. The cell was provided with two capillary side arms for filling; these were fitted with ground glass caps.

Filters.—To remove infra-red, a 1-cm. layer of 6% copper sulfate solution was used.[8] To isolate λ4358, a 4-mm. piece of Corning G 585

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[7] W. C. Bray, Z. *physik. Chem.*, 54, 592 (1906).

[8] W. W. Coblentz, ***Bur. Standards Bull.*, *9*,** 110 (1913).

was followed by a 2-mm. piece of Noviol A. On being photographed with a spectrograph, the radiation transmitted by these filters showed in addition to 4358 only the weak neighboring lines 4347 and 4339. To isolate 4047, a 1-cm. layer of 4% quinine hydrochloride was followed by a 5-mm. piece of Corning G 586 Å. Spectrographs of the radiation transmitted by this filter showed a trace of 4358 and various other lines down to 3900; most of the intensity, by far, was in 4047.

Spectroscopic Experiments.—Using a two-prism glass spectrograph we have photographed the absorption spectrum of chlorine monoxide in carbon tetrachloride solution. In agreement with Bowen the absorption was found to set in appreciably in the blue and to increase continuously toward the violet. After strong illumination of the solution with either white light or the line 4358 Å., a series of well-marked maxima of absorption situated at about 4350, 4240, 4130, 4020,... Å. developed. Since these absorption maxima are not attributable to chlorine, their source was sought in chlorine dioxide. It was found that chlorine dioxide solutions gave maxima in the same positions as the illuminated chlorine monoxide solutions; a 0.0015 molal chlorine dioxide solution showed the maxima to about the same extent as a 0.034 molal chlorine monoxide solution which had been exposed for three hours to our source of 4358 Å.

These experiments show that chlorine dioxide is produced in carbon tetrachloride solution by the illumination of chlorine monoxide but give only a rough suggestion of the quantity. We have accordingly attempted to estimate the number of molecules of chlorine dioxide produced per quantum absorbed and, taking account of the presence of chlorine dioxide, to reexamine the quantum yield in the decomposition of chlorine monoxide.

Absorption Coefficients.—Absorption coefficients of carbon tetrachloride solutions of chlorine, chlorine monoxide and chlorine dioxide were determined for the radiations 4358 and 4047 Å. Light from the mercury arc was passed through one of the filters described above, collimated, passed through a cell containing the solution, and then allowed to fall on a Moll thermopile connected with a galvanometer. The cell was removed and immediately replaced by a sheet of the same pyrex glass of which the cell was constructed. The ratio of the galvanometer readings for the two cases was taken as the transmission, I/I_0, of the solution. In Table I are given average values of the transmission for various solutions together with the absorption coefficients, a, defined by the equation

$$-\log_{10} I/I_0 = \alpha C$$

where C is the concentration in moles per liter. As our photochemical experiments were made in the same cell that was used for the absorption coefficients, these values are sufficient for our purpose. The thickness of the cell was 1.06 cm., so that the absorption coefficients, ϵ, defined by the equation

$$-\log_{10} I/I_0 = \epsilon C d$$

where d is the thickness of the cell in centimeters, are $\alpha/1.06$. In the case of chlorine, absorption coefficientswere also measured at the wave lengths 4358 Å. using a spectrograph and calibrated wire screens substantially as described by Winther.[9] The value of α obtained by this method, 2.40, is in agreement with that given in Table I.

TABLE I

ABSORPTION COEFFICIENTS IN CARBON TETRACHLORIDE SOLUTION

Substance	Moles per liter	Wave length, Å.	I/I_0	a
Cl_2	0.214	4358	0.308	2.40
	.0457	4047	.481	6.95
Cl_2O	.0229	4358	.671	7.60
	.0676	4358	.296	7.82
	.0789	4358	.247	7.70
	,0229	4047	.686	7.13
	.0676	4047	.336	6.99
ClO_2	.00115	4358	.595	197
	,00135	4358	.530	203
	.00115	4047	.195	616
	.000428	4047	.551	605

Method of Analysis.—The carbon tetrachloride solutions, which in the general case were presumed to contain chlorine, chlorine monoxide and chlorine dioxide, were treated in the following manner. A weighed amount of the solution was run into a flask containing an excess of potassium iodide acidified with a known excess of standard acid. The iodine liberated by the following reactions was titrated with thiosulfate

$$Cl_2 + 21- = I* + 2Cl^-$$
$$Cl_2O + 41- + H_2O = 2I_2 + 2OH^- + 2Cl^-$$
$$ClO_2 + 51- + 2H_2O = 5/2I_2 + 4OH^- + Cl^-$$

The unused excess of acid was then determined by adding a small amount of potassium iodate and titrating with thiosulfate the iodine liberated by the reaction

$$IO_3^- + 51- + 6H^+ = 3I_2 + 3H_2O$$

Calling a the number of equivalents of thiosulfate used per liter of sample in the first titration, and b the number of equivalents of acid neutralized per liter of sample as determined by the second titration, it is evident that

$$a = 2(Cl_2) + 4(Cl_2O) + 5(ClO_2) \qquad (1)$$
$$b = 2(Cl_2O) + 4(ClO_2) \qquad (2)$$

where the parentheses indicate molal concentrations.

In those cases (as in the absorption measurements or at the beginning of the photochemical exposures) where one or more of the three substances was known to be absent, these titrations sufficed; but when all three substances were present, an additional independent relation between their

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[9] C. Winther, Z. *wiss.* Phot., 22, 125 (1923).

concentrations was necessary. This was afforded by a measurement of I/I_0, the fraction of light transmitted by the solution when placed in the cell used for determining the absorption coefficients. The additional relation is, then

$$-\log I/I_0 = \alpha_1(\mathrm{Cl_2}) + \alpha_2(\mathrm{Cl_2O}) + \alpha_3(\mathrm{ClO_2}) \tag{3}$$

Simultaneous solution of Equations 1, 2 and 3 would give the desired analysis.

In practice it was found convenient to proceed slightly differently by using for the transmission measurements the radiation 4047 Å. For this wave length, the absorption coefficients of chlorine and chlorine monoxide are practically equal and much smaller than the coefficient for chlorine dioxide. If then no chlorine be allowed to escape from the solution during the photochemical reaction, any change in the transmission of the solution is ascribable to a change in $(\mathrm{ClO_2})$. If the solution initially contains no chlorine dioxide and has a transmission $(I/I_0)_i$, the concentration of chlorine dioxide corresponding to the transmission $(I/I_0)_t$ found after illumination is given by

$$-\log (I/I_0)_t + \log (I/I_0)_i = \left(\alpha_3 - \frac{\alpha_1}{2}\right)(\mathrm{ClO_2}) \tag{4}$$

From Table I, $[\alpha_3 - (\alpha_1/2)]$ has the value 607. We have accordingly followed, by transmission measurements, the concentration of chlorine dioxide in a sample of chlorine monoxide under illumination; using the final value of $(\mathrm{ClO_2})$ so obtained, we have determined the values of $(\mathrm{Cl_2})$ and $(\mathrm{Cl_2O})$ at the end by titration.

The experiments themselves afford two controls on this method of analysis. (1) The total chlorine in the solution, given by $(a - b)$, should be the same before and after illumination; this was ordinarily found to be the case to 1% or better which, in view of the small samples involved, is probably satisfactory. (2) From the analysis of the final solution, its transmission for 4358 Å. may be calculated and compared with a measured value. The calculated and observed transmission for this wave length agreed on the average to about 3%.

Measurement of Quantum Yields.—The chlorine monoxide solution, prepared as previously described, was placed in a small all-glass container built like a wash bottle. The exit tube from this container was ground into one of the capillary arms of the reaction cell. The cell was filled by blowing into the inlet tube of the container through a drying tube. The cell was then weighed, emptied into the titration flask, reweighed and immediately refilled. The initial composition of the $\mathrm{Cl_2O}$ solution was then determined by titration of the first sample. The second sample was then illuminated with 4358 Å. During this illumination, the cap C (Fig. 1) was removed to give a larger light source.

The illumination was interrupted at intervals for the measurement of

(1) the transmissions of 4358 and of 4047 and (2) the intensity of the 4358 as used for the reaction. The transmissions were measured as previously described. The light intensity was measured by noting the galvanometer deflection with C removed and the glass plate K in front of the thermopile; in this case a shunt was placed across the galvanometer to keep the deflection on the scale.

The thermopile had been calibrated with the aid of a carbon lamp calibrated by the Bureau of Standards; in the thermopile calibration the quartz window, L, was removed from the thermopile and the shunt from the galvanometer. The effect of the shunt had been determined by noting the deflections produced by a convenient white light source with and without the shunt.

The total number of quanta, Q, entering the reaction mixture in *t* minutes was calculated by the following formula

$$Q = 60t \times d \times f_1 \times f_2 \times f_3 \times E \times A \times f_4 \times f_5 \times q = 9.2 \times 10^{15} \times t \times d$$

d = galvanometer deflection in centimeters of scale as read with the shunt
f_1 = ratio of deflection without shunt to that with shunt
f_2 = rato of deflection with thermopile in plane of diaphragm and at its center. to deflection with thermopile in position used (the beam was slightly convergent) = 0.942
f_3 = ratio of average deflection over area of diaphragm to deflection with thermopile at center of diaphragm = 0.925
E = intensity of radiation giving unit scale deflection; ergs per sq. mm. per sec. per cm. scale deflection = 0.672
A = area of diaphragm opening in sq. mm. = 573
f_4 = reciprocal of transmission of quartz plate = 1.065
f_5 = reciprocal of transmission of one surface of pyrex plate = 1.035
q = number of quanta in one erg of radiation of wave length 4358 Å. = 2.217×10^{11}

The results of a number of experiments made by illuminating pure or nearly pure chlorine monoxide solutions of various concentrations are given in Table II. The initial and final amounts of chlorine monoxide and chlorine in the solutions are given in Cols. 3 and 4. The amount of solution was always 6.92 ± 0.02 cc. The amounts of chlorine dioxide present at various times (as computed from the transmission of λ4047) are given in Col. 5.

The total number of quanta having been absorbed by the system up to the time *t* (Col. 2) is given in Col. 9 and was calculated as follows. The number of quanta entering the reaction vessel in each interval of time was calculated from the average galvanometer deflection for that interval (Col. 8) as described above. This number was multiplied by $[1 - (I/I_0)]$ $[1 + r(I/I_0)]$ to give the number of quanta absorbed in the time interval. Here (I/I_0) is the average value of the transmission for λ4358 for the interval and ?(= 0.035) is the fractional reflection of radiation back into the cell at the rear window. (It may be noted that the small correction

TABLE II

QUANTUM: YIELD MEASUREMENTS

Expt.	Total time of ill. min.	Cl_2O, milli-moles	Cl_2, milli-moles	ClO_2 milli-moles	I/I_0 for 4358 Å.	I/I_0 for 4047 Å.	Av galv. defl for preceding interval	Total quanta abs. × 10^{-19}	Cl_2O decomp per quantum abs by soln	Cl_2O decomp per quantum abs by Cl_2O
1	0	0.158	0.000	0.00000	0.676	0.686	..	..	..	..
	170	..	..	.00338	..	.346	20.7	1.22	..	..
	240	.123	.035	,00399	.546	,306	18.7	1.76	1 20	1.72
2	0	.215	.005	.00000	.574	.579	..	..	..	..
	60	..	..	,00225	..	.367	26 9	0.675	..	..
	120	..	..	,00370	..	.275	22 2	1.28	..	..
	180	,176	.042	.00475	.454	.222	22.8	1.95	1.21	1 65
3	0	.375	.004	.00000	.383	.414	..	..	..	
	30	..	..	.00225	.347	.270	22.2	0.394	..	..
	60	.352	.023	,00409	,315	.182	26 0	0.881	1.58	1.83
4	0	.298	.025	00000	.462	.476	..	...	..	..
	30	..	..	.00164	.430	.342	20 2	0.313	..	..
	60	..	..	.00303	,402	.258	18 5	0.616	..	..
	90	.276	.044	.00394	.385	.215	16 7	0.900	1.48	1.77
5	0	.280	.006	.00000	.491	.510	..	...	..	..
	60	..	..	.00238	.439	.316	18.9	0.567	..	..
	120	..	..	.00449	.396	.206	25.5	1.40	..	..
	180	..	..	.00572	.369	.161	21.4	2.14	..	..
	240	.222	.059	.00714	.355	,121	22.5	2.94	1.20	1.70
6	0	.100	.006	.00000	.778	.781	..	...	..	..
	30	..	..	.00085	.745	.657	26.2	0.176	..	..
	60	..	..	.00138	.724	.592	25.7	0.363	..	..
	90	..	..	.00180	.707	.545	25.8	0.563	..	..
	120	,083	.018	.00214	.702	.507	25.6	0.776	1.33	1.82

$r(I/I_0)$ for rear-window reflection is not compensated in the absorption measurements.) The sum of the quanta absorbed in all intervals up to the time t is given in Col. 9.

The amount of chlorine dioxide formed in the various runs is shown in Fig. 2 plotted against the number of quanta absorbed. In a given run, the amount of chlorine dioxide formed increases less and less rapidly with the quanta absorbed as the exposure is prolonged. At least two reasons may be given for this: (1) chlorine dioxide already formed acts as an internal filter and partially screens its further formation; (2) chlorine dioxide is itself decomposed photochemically.[10] In addition there is the possibility of photochemical reaction between chlorine dioxide and chlorine monoxide.

When the various runs are compared with each other, it is found that for a given number of quanta absorbed, more chlorine dioxide has been formed the higher the initial concentration of chlorine monoxide. This effect

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[10] H. Booth and E. J. Bowen, *J. Chem. Soc.*, 127,510 (1925).

again could obviously result from internal screening in both the formation and decomposition of the chlorine dioxide.

The simplest conditions evidently prevail at the beginning of the exposure where the material is substantially all chlorine monoxide. The initial (quantum) rate of formation of chlorine dioxide appears to be not markedly, if at all, dependent on the concentration of chlorine monoxide. The initial slope of the curves gives directly a quantum yield of about **0.35** chlorine dioxide formed per quantum absorbed.

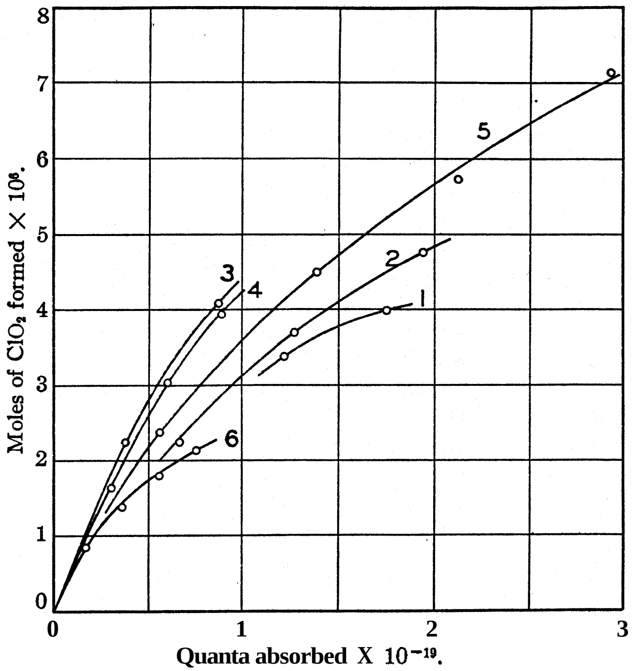

Fig. 2.—Amount of ClO_2 formed *vs.* number of quanta (4358 Å.) absorbed. The numbers on the curves are the experiment numbers of Table II. The initial concentrations of Cl_2O increase in the order 6, 1, 2, 5, 4, 3.

Our method of analysis supplied a knowledge of the chlorine monoxide present at only the beginning and end of a run. The number of molecules of chlorine monoxide decomposed in each entire run per quantum absorbed, irrespective of the absorbing substances, was computed from Cols. **3** and 9 and is given in Col. **10.** It may be seen that in Expts. **3** and 4, where the exposures were shortest and the proportion of chlorine dioxide at the end smallest, the yields were highest, *viz.*, 1.58 and 1.48, as against values around **1.2** in longer exposures. This suggests that shorter exposures would lead to still higher values for the initial yield; for after the decomposition of only a small amount of chlorine monoxide, the chlorine dioxide which had been formed played a considerable part in the light absorption. However, on account of the small titration differences already involved, experiments resulting in smaller decompositions did not appear feasible.

We have, therefore, calculated the number of molecules of chlorine monoxide decomposed per quantum absorbed by the chlorine monoxide. At any moment, the fraction of the absorption due to chlorine dioxide is $\alpha_3(ClO_2)/[\alpha_1(Cl_2) + \alpha_2(Cl_2O) + \alpha_3(ClO_2)]$. The denominator is equal to $-\log.(I/I_0)$ for λ4358. Hence the fraction of the entering quanta which are absorbed by other than chlorine dioxide is

$$\left[1 - \frac{\alpha_3(ClO_2)}{-\log\,(I/I_0)}\right][1 - I/I_0][1 + r(I/I_0)]$$

Values of this last expression were calculated for each time interval using average values of (ClO_2) and (I/I_0); these were multiplied by the number of quanta entering in the interval and summed over the entire run. The ratio of the number of molecules of chlorine monoxide decomposed to this sum is given in Col. 11. Strictly this is the yield per quantum absorbed by $Cl_2O + Cl_2$; however, the quantity of free chlorine was never large and its absorption coefficient for 4358 is small. These yields are comparatively constant, showing possibly a slight tendency to increase with decreasing exposure; the mean for the three longest runs is 1.69, while the mean for the three shortest runs is 1.81. In view of the uncertainty of extrapolation and of the small titration differences, it seems not impossible that the value for zero exposure and hence for pure chlorine monoxide solution may be as high as 2.

Summary

The effect of light of wave length 4358 Å. on solutions of chlorine monoxide in carbon tetrachloride has been investigated. It has been found that the decomposition of chlorine monoxide is accompanied by the formation of considerable chlorine dioxide. In solutions 0.014 to 0.054 molal in chlorine monoxide, the initial rate of formation of chlorine dioxide has been found to be about 0.35 molecule of chlorine dioxide per quantum absorbed. The initial rate of decomposition has been found to be at least 1.8 molecules of chlorine monoxide per quantum absorbed.

PASADENA, CALIFORNIA

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

THE INTERACTION BETWEEN NITROGEN TRICHLORIDE AND NITRIC OXIDE AT −150". II. FURTHER EVIDENCE FOR THE FORMATION OF NITROGEN DICHLORIDE AND OF MONO-OXYGEN-DINITROGEN-DICHLORIDE

BY WILLIAM ALBERT NOYES

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In a paper published two years ago[1] it was shown that at −80°, in a solution of chloroform and carbon tetrachloride, two moles of nitric oxide react with one mole of nitrogen trichloride, giving one mole of nitrosyl chloride, one of nitrous oxide and two atoms of chlorine

$$2NO + NCl_3 = NOCl + N_2O + Cl_2$$

This was explained by assuming that the nitric oxide, having an odd electron, takes an atom of chlorine with an odd electron from the nitrogen trichloride to form the nitrosyl chloride. This leaves nitrogen dichloride with an odd electron and the latter combines with another mole of nitric oxide to form mono-oxygen-dinitrogen-dichloride, $O{=}N{-}NCl_2$. This last compound dissociates at −80°, giving nitrous oxide and chlorine. It was also found that at −130 to −140°, in petroleum ether, the reaction corresponds to the equation

$$NCl_3 + NO = N_2O + 3Cl$$

probably because hydrochloric acid formed by the action of nitrogen trichloride on the petroleum ether catalyzes a reaction between the nitrosyl chloride first formed and nitrogen trichloride, giving nitrous oxide and chlorine. It should be remarked, however, that this equation represents the final result of at least three or four reactions which occur consecutively or simultaneously.

To simplify the conditions and to eliminate, as far as possible, the catalytic effect of the hydrochloric acid and the reactions between nitrosyl chloride and nitrogen trichloride and between nitric oxide and chlorine, the reactions have been carried out in the presence of chloroform and carbon tetrachloride at −150°, the boiling point of nitric oxide.

Experimental Part

The apparatus used, shown in Fig. 1, was the same as that described in the first paper except that the bulb, F, in which the reaction was carried out, was surrounded with a second bulb sealed to it as shown in Fig. 2. Nitric oxide from a glass gasometer containing about 12 liters was condensed in the outer bulb by immersing it in liquid air. In some cases the solution containing a known amount of nitrogen trichloride was introduced by distilling it under low pressure from a glass bulb in which it had been frozen before

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[1] Noyes, THIS JOURNAL, 50,2902 (1928).

connecting it with the apparatus at E. As the mixture distilled into the reaction bulb F, which was kept in liquid air, it froze on the walls of the bulb. In other cases the solution was allowed to flow slowly through a fine capillary tube down the inner wall of F. The latter method is considered better. This gave a large reacting surface for the mixture, and as the freezing point of nitrogen trichloride is lower than that of the mixture of chloroform and carbon tetrachloride, the trichloride was largely on the outside of the surface of the crystals of the solvent.

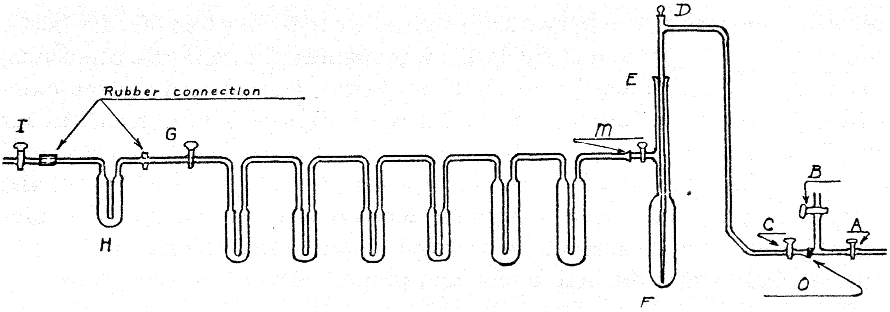


Fig. 1.—Ground-glass joints at O, E and M.

After evacuating the bulb, introducing nitrogen and evacuating again three or four times to remove the air, the liquid air was lowered away from the outer bulb containing liquefied and frozen nitric oxide. By proper adjustment of the cylinder containing the liquid air, the nitric oxide in the outer bulb was allowed to evaporate slowly back into the gasometer. In this manner a constant temperature of approximately −150° could be maintained almost indefinitely.

A measured quantity of nitric oxide was then slowly introduced through A and C (Fig. 1). The reaction, which did not always begin immediately, was apparent from the change in color of the mixture to the red color of nitrosyl chloride. After the desired amount of nitric oxide had been introduced, the mixture was allowed to stand for some time at −150° until the reaction was complete.

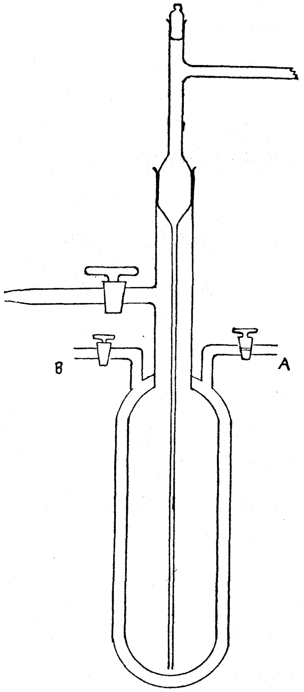


Fig. 2.

A large number of experiments at −150° have been carried through and various changes in the technique of separating the products of the reaction have been tried. The most important change has been measuring the nitrous oxide instead of weighing it. After fractionating the products and condensing the nitrous oxide in the U-tube H (Fig. 1), immersed in liquid air, the tube was connected with a tube leading to the bottom of a dry bottle and a tube from the top of the latter was connected to a bottle containing water in such a manner that as the nitrous oxide was allowed to evaporate, after removing the liquid air in which the U-tube was immersed, the air displaced passed into the second bottle and displaced its own volume of water. The water displaced was measured and thus the volume of the nitrous oxide was determined without allowing the gas to come in contact with water. Small amounts of nitrosyl chloride and chlorine present in the nitrous oxide were determined and proper corrections were made.

Two experiments at −80° were made to test the results given in the first paper by the new technique.

Attempts to carry out the reaction at the temperature of liquid air, −185 to −191°, have not been successful. After 11.9 millimoles of nitric oxide had stood in contact with the mixture containing an excess of nitrogen trichloride, at that temperature, for forty-five hours, 9.4 millimoles were recovered unchanged.

Results and Discussion.—From a large number of experiments, two at −80° and three at −150° have been selected as representing, approximately, the course of the reaction, which is distinctly different at the two temperatures.

TABLE I

RESULTS OF EXPERIMENTS

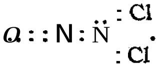
NCl_3 recovered	NCl_3 reacting	Molecular ratios NO				Temp., °C.
		NO	N_2O	NOCl	Cl	
0.04	1	1.96	0.71	1.01	2.20	−80
.23	1	2.42	.85	1.16	1.5	−80
.32	1	2.94	.72	1.70	0.16	−150
.33	1	3.10	.92	2.10	.60	−150
.23	1	3.00	.95	1.70	.90	−150

The results at −80° confirm the equation given in the first paper, $NCl_3 + 2NO = NOCl + N_2O + 2Cl$, as representing, approximately, the reactions which take place at that temperature.

At −150° the results correspond, approximately, to the equation

$$NCl_3 + 3NO = 2NOCl + N_2O + Cl$$

The results at −80° were explained by assuming that nitric oxide, having an odd electron, takes a chlorine atom with an odd electron from the nitrogen trichloride to form nitrosyl chloride. This leaves nitrogen dichloride, NCl_2, having an odd electron, which causes it to combine immediately with a second mole of nitric oxide to give mono-oxygen-dinitrogen-dichloride,



$\mathrm{O}::\mathrm{N}:\overset{\cdot\cdot}{\mathrm{N}}\begin{matrix}:\mathrm{Cl}\\:\mathrm{Cl}\end{matrix}$. Because of the oxygen combined with one of the nitrogen atoms, this compound seems to dissociate to nitrous oxide, ${}^{-}\!:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\overset{+}{\mathrm{N}}:::\mathrm{N}:$ and chlorine at −80°.

It seemed difficult, at first, to explain the formation of *two* moles of nitrosyl chloride at −150°, but further consideration has led to the conclusion that the mono-oxygen-dinitrogen-dichloride is sufficiently stable to maintain a brief existence at −150° and that it yields a second atom of chlorine with an odd electron to a second mole of nitric oxide, forming the second mole of nitrosyl chloride. This would leave mono-oxygen-dinitrogen-monochloride, $\underset{\cdot\cdot}{\ddot{\mathrm{O}}}::\ddot{\mathrm{N}}:\underset{\cdot}{\ddot{\mathrm{N}}}:\mathrm{Cl}$. This would dissociate to nitrous oxide and chlorine, either at once or during the subsequent distillation of the products.

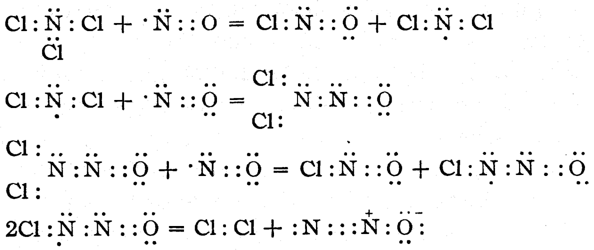
The course of the reaction at –SO° shows that nitric oxide and chlorine combine very slowly to form nitrosyl chloride at that temperature and the second mole of nitrosyl chloride is very unlikely to have come from that combination.

Summary

1. At −150° the interaction of nitrogen trichloride and nitric oxide proceeds, approximately, according to the equation

$$\mathrm{NCl_3 + 3NO = 2NOCl + N_2O + Cl}$$

2. This equation is thought to represent the result of four successive reactions which may be represented by the equations



$$\mathrm{Cl}:\underset{\underset{\displaystyle \mathrm{Cl}}{\cdot\cdot}}{\ddot{\mathrm{N}}}:\mathrm{Cl} + \cdot\ddot{\mathrm{N}}::\mathrm{O} = \mathrm{Cl}:\ddot{\mathrm{N}}::\underset{\cdot\cdot}{\ddot{\mathrm{O}}} + \mathrm{Cl}:\underset{\cdot}{\ddot{\mathrm{N}}}:\mathrm{Cl}$$

$$\mathrm{Cl}:\underset{\cdot}{\ddot{\mathrm{N}}}:\mathrm{Cl} + \cdot\ddot{\mathrm{N}}::\underset{\cdot\cdot}{\ddot{\mathrm{O}}} = \begin{matrix}\mathrm{Cl}:\\ \\ \mathrm{Cl}:\end{matrix}\ddot{\mathrm{N}}:\ddot{\mathrm{N}}::\underset{\cdot\cdot}{\ddot{\mathrm{O}}}$$

$$\begin{matrix}\mathrm{Cl}:\\ \\ \mathrm{Cl}:\end{matrix}\ddot{\mathrm{N}}:\ddot{\mathrm{N}}::\underset{\cdot\cdot}{\ddot{\mathrm{O}}} + \cdot\ddot{\mathrm{N}}::\underset{\cdot\cdot}{\ddot{\mathrm{O}}} = \mathrm{Cl}:\ddot{\mathrm{N}}::\underset{\cdot\cdot}{\ddot{\mathrm{O}}} + \mathrm{Cl}:\underset{\cdot}{\ddot{\mathrm{N}}}:\ddot{\mathrm{N}}::\underset{\cdot\cdot}{\ddot{\mathrm{O}}}$$

$$2\mathrm{Cl}:\underset{\cdot}{\ddot{\mathrm{N}}}:\ddot{\mathrm{N}}::\underset{\cdot\cdot}{\ddot{\mathrm{O}}} = \mathrm{Cl}:\mathrm{Cl} + :\mathrm{N}:::\overset{+}{\mathrm{N}}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}{}^{-}\!:$$

3. Attempts to isolate the intermediate products, nitrogen dichloride, mono-oxygen-dinitrogen-dichloride and mono-oxygen-dinitrogen-monochloride have not been successful.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 7]

THE PREPARATION OF SULFUR HEXAFLUORIDE AND SOME OF ITS PHYSICAL PROPERTIES

BY WALTER C. SCHUMB AND E. LEE GAMBLE

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The object of the present research was to investigate in somewhat greater detail than previously has been described the preparation and purification of sulfur hexafluoride, as well as to determine certain of its physical properties which appeared to be in need of revision. Because of the increasing attention which is being given to certain gaseous fluorides as well as the rather unusual intrinsic characteristics of sulfur hexafluoride, it was thought desirable to communicate the results of our study thus far established. Sulfur hexafluoride is a gas at ordinary temperature; it solidifies at low temperature, melting at −50.8°. Its vapor pressure at that temperature is above atmospheric; it must be cooled further, to −63.8°, to lower the pressure to 760 mm.; the determination of these temperatures and pressures was one of the objects of this work.

The Generation of Fluorine.—The only practical method of preparation of sulfur hexafluoride is the combustion of sulfur in fluorine, so that a brief account of our experience with the generation of fluorine would not appear to be out of place here. Since Moissan's[1] first preparation of this gas by the electrolysis of a solution of potassium fluoride in anhydrous hydrogen fluoride, using a U-tube and electrodes of platinum–iridium, much improvement in the design and operation of fluorine generators has been attained. Of various types of generators, such as those of F. Meyer and Sandow,[2] J. Simons,[3] Lebeau and Damiens,[4] and Bancroft and Jones,[5] that described by the last-named investigators is representative of recent practice. Their generator is an improved form of that first described by W. L. Argo,[6] the essential change being in the use of magnesium metal in place of copper for the containing vessel and diaphragm.

In starting the present work, several types of fluorine generators using fused electrolytes were constructed and the unsuitability of copper for the containing vessel and diaphragm was soon established. The generator finally adopted and successfully operated over an extended period of time was a modification of that described by Bancroft and Jones, with one

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[1] Moissan, *Compt. rend.*, 53, 202 (1886).

[2] F. Meyer and Sandow, *Ber.*, 54, 759 (1921).

[3] J. Simons, THIS JOURNAL, 46, 2175 (1924).

[4] Lebeau and Damiens, *Compt. rend.*, 181, 917 (1925).

[5] Bancroft and Jones, *Trans. Am. Electrochem. Soc.*, 55, 71 (1929).

[6] Argo, Mathers, Humiston and Anderson, *J. Phys. Chem.*, 23, 348 (1919).

important difference: welded 3.2 mm. monel metal was used in place of magnesium in the construction of the vessel and diaphragm. After more than one hundred and fifty hours of operation at 220 to 300° there has been no appreciable attack of the monel by the fused electrolyte—KHF_2— and only a slight attack of the graphite anode.

Electrical connection was made to the graphite anode by means of a 3.2-mm. copper wire threaded at the end and screwed tightly into the 2.54-cm. graphite rod, the whole being held at the top of the diaphragm by a "stopper" of Portland cement. A horizontal copper disk attached to the lead wire served as a shield to prevent spray from entering and clogging the outlet tube. The bottom of the diaphragm was closed with a removable monel disk held snugly to the diaphragm by three flat hooks brazed to the latter. Three rows of eight 6.4 mm. holes perforated the lower end of the diaphragm. The current employed varied from 12 to 15 amp.; the potential drop across the cell averaged 3 to 4 volts. The generator held approximately 3.6 kilos of electrolyte, which was melted in a large copper beaker before pouring into the generator, wherein it was kept molten by means of a nichrome heating coil wound about the vessel. When a run was interrupted, the electrolyte was poured out into the copper beaker, in which it solidified. When the electrolysis was resumed the cake was dislodged, broken into large lumps, remelted and again poured into the generator. The fluorine contains some hydrogen fluoride, oxygen and probably a little carbon tetrafluoride. As far as the satisfactory functioning of the generator is concerned, our experience confirms the observations of others in that the water content of the electrolyte has much to do with successful operation. As electrolysis proceeds—at as low a temperature as possible, in order to minimize vaporization of hydrogen fluoride—the water is gradually eliminated.

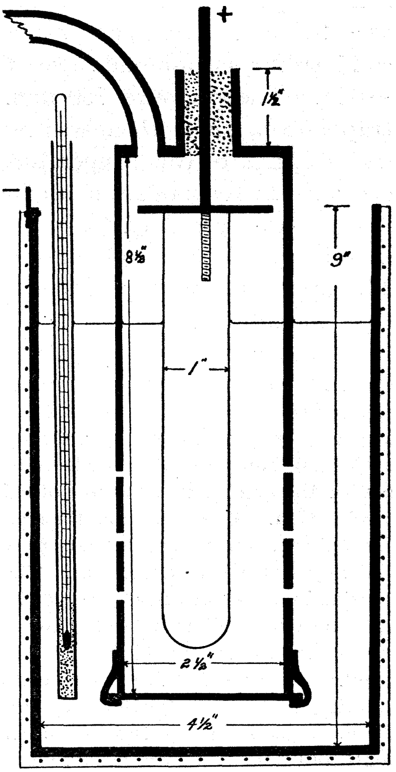

Fig. 1.—Fluorine generator.

The Preparation of Sulfur Hexafluoride and Previous Work.—Moissan and Lebeau[7] discovered that when sulfur burns in fluorine the chief product of the reaction is the gas, sulfur hexafluoride, colorless, odorless and very inert under ordinary conditions. Of this substance they say that "it solidifies at about −55° to a white, crystalline mass, which liquefies and boils at a temperature but little removed from its melting point." In determining the density of the gas, Moissan and Lebeau used a method

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[7] Moissan and Lebeau, *Compt. rend.*, 130, 865 (1900); *Ann. chim. phys.*, [7] **26**, 147 (1902).

previously described by Moissan and Gautier,[8] which consisted of the comparison of the weights of equal volumes of sulfur hexafluoride and of air taken under the same conditions. Four values were given: 4.95, 4.99, 5.09 and 5.11; average 5.03.

Prideaux[9] later made a comparative study of the physical properties of the hexafluorides of sulfur, selenium and tellurium. The sulfur hexafluoride had been purified by three distillations. He determined the melting point of sulfur hexafluoride as −56 to −55°, the boiling point as −62° at 760 mm., and made a determination of the vapor pressure of solid sulfur hexafluoride over the temperature interval −110° to about −65°. The pressure, 760 mm. at −62°, was calculated by a short extrapolation, since there was not enough sulfur hexafluoride to continue the readings to this temperature. The data were not tabulated but were given in the form of a smooth curve. The temperature of the sulfur hexafluoride was assumed to be the same as that of the ether (cooled with liquid air, and gradually allowed to warm up) that surrounded the bulb. The apparatus was quite small because of the small amount of the substance available.

The method of preparation of sulfur hexafluoride used in the present investigation was as follows. The fluorine from the generator passed through two copper U-tubes coupled thereto and filled with flakes of freshly fused potassium fluoride to remove some of the hydrogen fluoride, then through a 2.5-cm. copper tube about 50 cm. long filled with small lumps of sulfur. The sulfur ignites immediately in the fluorine and the progress of the combustion can be noted by the heating of the copper tube at the zone of combustion. The gases from the reaction tube passed through a long column of freshly fused potassium hydroxide flakes to remove the greater part of lower fluorides of sulfur and any sulfur dioxide present. The gas was now collected over 3 N potassium hydroxide in a 20-liter carboy, the solution being siphoned out as the carboy filled with gas, and the whole allowed to stand for several days with occasional shaking. From the carboy the gas was passed at a rate of about 1.5 liters per hour through a trap cooled to approximately −60° to remove much of the water vapor, through a column of calcium chloride, and then through two absorption bottles containing anhydrous alcohol. Next the gas passed through two absorption bottles containing water and one containing concentrated sulfuric acid to remove alcohol vapor, and finally was solidified by strong cooling in the first of a series of four bulbs. The quantity of solid so obtained was about 80 g. The solid was now repeatedly sublimed, each operation requiring from five to seven hours and approximately one-third (the first and last portions) of each fraction being discarded. Finally the bulb of the vapor pressure apparatus was well evacuated, cooled with liquid air, and the sulfur hexafluoride sublimed directly into it.[10]

Vapor Pressure of Sulfur Hexafluoride.—The apparatus shown in Fig. 2 was employed in the vapor pressure measurements. The purpose of the compressed air, mercury reservoir and stopcocks attached thereto was to make possible the adjustment of

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[8] Moissan and Lebeau, *Compt. rend.*, 130, 984 (1900); Moissan and Gautier, *Ann. chim. phys.*, [7] 5, 568 (1895).

[9] Prideaux, *J. Chem. Soc.*, 89, 323 (1906).

[10] It was observed that at the temperature of liquid air the vapor pressure of solid sulfur hexafluoride is certainly less than 0.01 mm.

the mercury level in the short arm to the same point when taking readings, so that the work could be carried out at constant volume. The scale was a metal tape, one inch wide, graduated in millimeters. The bulb containing the sulfur hexafluoride was cooled with a mixture of alcohol and solid carbon dioxide in a one-liter Dewar flask. The temperature of this bath was taken as the temperature of the sulfur hexafluoride. This was justifiable for several reasons: (1) the bath in some runs was allowed to warm up very slowly from one point to the next, not less than six hours being taken for a temperature interval of 25°; (2) as will be described presently, the bath could be held at a given temperature for ten or fifteen minutes without further change in pressure; (3) check pressure readings could be obtained with falling temperature. The bath was kept well stirred throughout by means of a motor-driven stirrer. By the gradual addition of cold alcohol–carbon dioxide mixture to the bath it was possible to keep the temperature constant (within approximately 0.1°), or by regulating the rate of addition, to lower the temperature stepwise and thus reach equilibrium from the upper side.

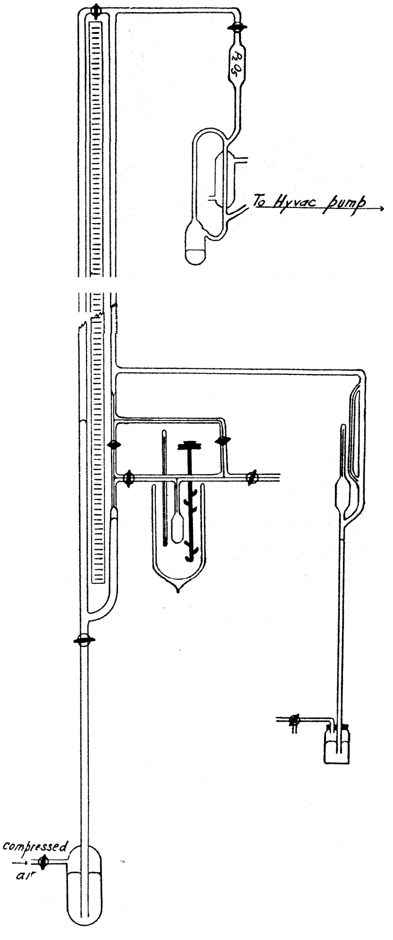

Fig. 2.

Seven runs were made on the vapor pressure, the results of which are shown in the accompanying table and graph. The values designated as "Experimental Data" in the table represent, in general, the mean of several determinations at the given temperatures; from these results the smooth curve was constructed, and from the graph, in turn, the interpolated values given in the table were obtained. By interpolation, likewise, the temperature at which the vapor pressure of solid sulfur hexafluoride becomes 760 mm. was found to be −63.8°. In the individual runs a check upon the purity of the substance was obtained by permitting successive fractions of the same to vaporize, measurements being taken before and after the vaporization. In three runs, beginning with the solid at the lowest temperature (about −72°), the vapor pressure readings were made at intervals with very slowly rising temperature, and were extended well above the melting point (−50.8'); readings were then taken while the substance was cooled slowly, thus passing from the liquid to the solid state. Further evidence of the purity of the substance is afforded by the fact that the measurements recorded were made upon two entirely different samples of sulfur hexafluoride, independently prepared and purified.[11]

TABLE I

VAPOR PRESSURE OF SULFUR HEXAFLUORIDE

Experimental data				Interpolated from graph	
Temp., °C.	Press., mm.	Temp., °C.	Press., mm.	Temp., °C.	Press., mm.
−72.4	433	−58.3	1081	−72.0	445
−71.4	460	−57.5	1141	−70.0	506
−70.9	471	−56.0	1248	−68.0	578
−69.1	535	−54.8	1335	−66.0	660
−67.8	588	−53.1	1472	−64.0	749
−67.0	628	−52.0	1581	−62.0	849
−66.6	635	−51.1	1655	−60.0	966
−65.5	686	−50.1	1745	−58.0	1099
−64.4	734	−49.7	1772	−56.0	1247
−63.8	766	−49.1	1834	−54.0	1405
−62.5	827	−47.8	1928	−52.0	1577
−61.7	867	−46.8	2007	−51.0	1675
−60.8	921	−46.4	2054	−50.0	1745
−59.8	976			−49.0	1820
				−48.0	1892
				−47.0	1987
				−46.0	2090

Melting Point of Sulfur **Hexafluoride.**—The melting point of sulfur hexafluoride as given by Moissan is −55° and by Prideaux −56 to −55°. This value could not be checked by us either from the interpretation of the vapor pressure curves or by direct observation of the melting and solidification of a small quantity of the substance contained in a sealed bulb. The melting point of our purified product thus observed was found to be −50.8 ±0.2°, this value being checked repeatedly. The melting point as indicated by the break in the vapor pressure curve is in fair agreement with this value, but inasmuch as the change of slope at the triple point is so slight, the precise location of the break in the curve is uncertain. Consequently, the value given is based mainly upon the result of direct observation of the melting point. The low values of the earlier observers we feel were due to the presence of impurities. This is also reflected in the case of the gas density determinations which follow.

Density of Gaseous Sulfur **Hexafluoride.**—The density of gaseous sulfur hexafluoride was determined at 20.0°, using the purified material employed in the vapor pressure work. The density globe of known weight and internal volume (495.56 cc.) was connected to the sulfur hexafluoride bulb, the latter immersed in liquid air, and the system evacuated to less

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[11] It may be worth noting that the pressure of the gas at room temperature becomes too great for ordinary glass apparatus, but there is no reason why liquid sulfur hexafluoride may not conveniently be stored in metal cylinders; the equilibrium pressure under ordinary conditions probably would not exceed greatly that of liquid ammonia.

than 0.001 mm. By allowing the sulfur hexafluoride to warm up the density globe was permitted to fill with the gas at a pressure of a little more than atmospheric. The globe was then removed and placed in a thermostat at 20.0° where it remained for at least fifteen minutes; the stopcock was then opened momentarily to bring the gas to atmospheric pressure and after another short interval again opened and closed, the barometer reading now being taken. The globe and sulfur hexafluoride were weighed by the counterpoise method, employing the usual precautions. The external volumes of counterpoise and globe differed by not more than 0.5 cc. The results given are corrected for the change in volume of the density globe on evacuation, and the pressures refer to mercury at 0°. For the sake of comparison with Moissan's determinations, the relative density referred to air is also given, calculated by assuming the average molal weight of air to be 28.98 and that sulfur hexafluoride behaves as a perfect gas over the interval involved. The theoretical value for sulfur hexafluoride is 5.04.

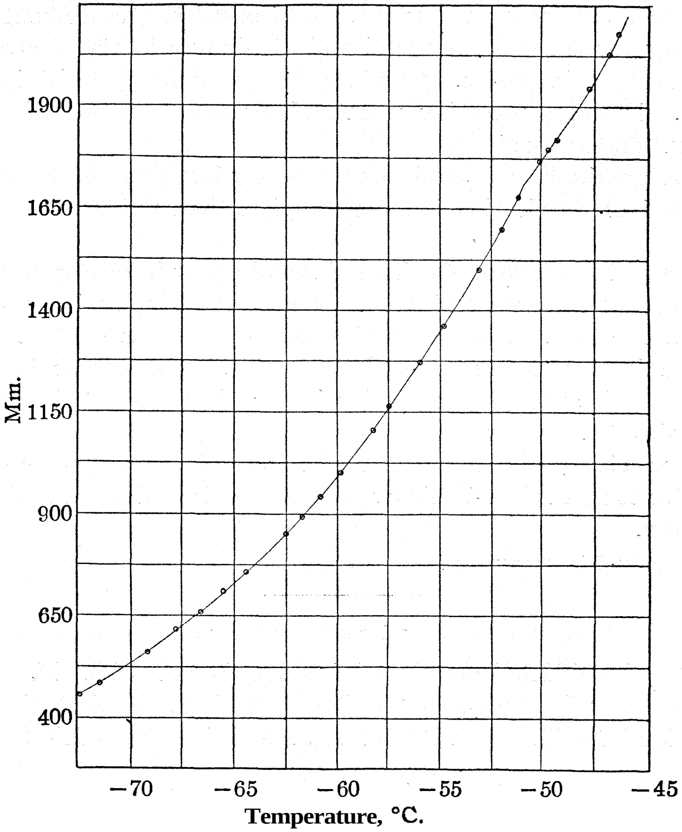

Fig. 3.—Vapor pressure of sulfur hexafluoride.

	Pressure, mm.	Density, g./liter at 20.0°	Relative density (air = 1)
I	753.5	6.091_7	5.101
II	753.5	6.094_9	5.10_3
III	760.5	6.164_6	5.11_4
			5.106 (mean)

Summary

1. In the preparation of fluorine, monel metal has been found entirely satisfactory for the cathode vessel and diaphragm in the electrolysis of fused potassium bifluoride. Graphite as the anode material is slightly attacked. Details concerning structural features and operation of the fluorine generator are given.

2. The synthesis and purification of sulfur hexafluoride are described; the method of purification is more complete than hitherto has been described.

3. The vapor pressure of solid and liquid sulfur hexafluoride has been measured up to three atmospheres, the temperature interval covered being from —72 to —45°. The pressure becomes 760 mm. at —63.8°.

4. The density of the gas at 20°, 753.5 mm., is found to be 6.093 g. per liter. From this the relative density (air = 1) is calculated to be 5.10_6; theoretical, 5.04.

5. The melting point of pure sulfur hexafluoride is found to be —50.8 ± 0.2°. This is more than 4° higher than the earlier values of Moissan and of Prideaux.

CAMBRIDGE, MASSACHUSETTS

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

DEFORMATION OF ELECTRON SHELLS. II. ABSORPTION SPECTRUM, MOLECULAR VOLUME AND REFRACTION OF CERTAIN RARE EARTH SALTS

BY P. W. SELWOOD

RECEIVED AUGUST 25, 1930 PUBLISHED NOVEMBER 5, 1930

In the first paper of this series[1] it was pointed out that there is a relation between the absorption spectrum and other properties of neodymium perchlorate. The object of the present work was to extend the observations to the nitrate and chloride of neodymium and, so far as possible, to other members of the rare earth group.

Experimental

The experimental procedure involved in the measurements described here will be given only wherein it differs from that already reported.

The quantitative analysis of neodymium nitrate solutions presented a

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[1] Selwood, THIS JOURNAL, 52,3112 (1930).

much simpler problem than either the perchlorate or the chloride. Weighed samples of the solutions were evaporated to dryness and ignited directly to the oxide. The whole analysis took less than an hour, and the results are believed to be accurate to 0.05%.

In the case of the neodymium chloride it was necessary to use the oxalate–oxide method as described for the perchlorate determination. In every case the filtrate from the neodymium oxalate was tested spectroscopically for neodymium, and the oxide, after being weighed, was dissolved in nitric acid and tested for chloride. The absence of chloride in any of the samples indicates that neodymium oxalo-chloride does not form in noticeable amounts if the rare earth is precipitated slowly from the hot, dilute solution, with fairly dilute oxalic acid. The chloride results are believed to be accurate to 0.1%.

The determinations of density and of refractive index were as described before. All the data on molecular refraction refer to the hydrogen C line. The molecular volumes were calculated as shown by Geffcken[2] from the relation

$$V = \frac{M}{d_0} - \frac{3000\,(d - d_0)}{N}$$

where V is molecular volume, M is molecular weight, d is density of the solution, d_0 is density of water and N is concentration in equivalents per 1000 cc. of solution.

In addition to the absorption bands of neodymium nitrate and chloride, an examination was also made of the spectrum of praseodymium, samarium, europium, gadolinium, holmium and erbium. In all cases the spectrum of a 10 N solution through a 3-mm. layer was compared with that of a 0.2 N solution through the equivalent thickness of 150 mm.

In the case of the gadolinium, which has no absorption bands in the visible region of the spectrum, the procedure was modified in that uranium salts placed in the positive crater of a carbon arc formed the source of ultraviolet illumination. The very large number of emission lines from uranium served in place of a continuous spectrum. It has recently been reported by Freed and Spedding[3] that gadolinium has some faint absorption lines in the visible region. In an effort to verify these results, the writer examined the spectrum of a 150-mm. layer of 10 N gadolinium nitrate, but no trace of selective absorption could be detected. The spectrum was photographed on a Hilger E 1 quartz prism spectrograph.

During the course of the work on neodymium nitrate solutions it seemed desirable to examine the absorption spectrum of a crystal of the same salt. Well-formed crystals were prepared from a saturated solution which was slowly evaporated. They were soft and easily broken, but several pieces

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[2] Geffcken, *Z. physik. Chem.*, *5B*, 81 (1929).

[3] Freed and Spedding, *Phys. Rev*,, 34, 945 (1929).

with smooth surfaces were obtained by rubbing the crystal down with the moist finger tip. In order to prepare a dilute solution of equivalent thickness with which to compare the spectrum of the crystal it was necessary to determine the concentration of neodymium nitrate in equivalents per 1000 cc. of crystal. This was done by analyzing a crystal for neodymium content by ignition to the oxide, and by finding the density through the loss of weight in benzene, in which neodymium nitrate is insoluble. Two such determinations gave 15.13 and 15.11 as the normality of $Nd(NO_3)_3$ in the crystals. The crystal finally used for the spectroscopic work had a thickness of 1.70 mm. This was equivalent to 100 mm. of 0.257 N solution with which it was compared.

The purity of the neodymium used has already been discussed. All the other rare earths except the praseodymium and the erbium had been prepared by the writer, some expressly for this work and some in connection with other work. The praseodymium contained 1% of lanthanum. The samarium showed no absorption bands of neodymium and no arc lines of europium. The europium, of which only a gram or two was available, was free from all other rare earths. The gadolinium contained only a spectroscopic trace of europium. The holmium and erbium material consisted largely of the colorless rare earth yttria. The first contained 26% holmium, and the second 20% erbium.

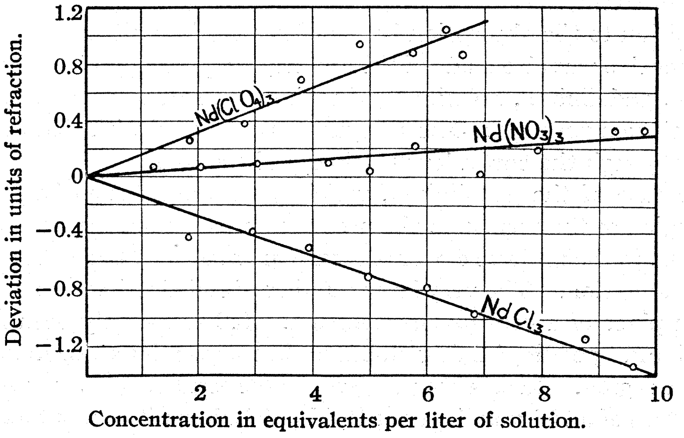


Fig. 1.—Deviations from additivity in the molecular refraction of neodymium perchlorate, nitrate and chloride in aqueous solution.

Results

The values for the molecular volume and refraction of neodymium nitrate and chloride are shown in Tables I and II. Figure 1 shows the deviations from additivity when the molecular refractions of the nitrate and chloride are plotted against concentration. For the sake of complete-

Table I

Molecular Volume and Reqraction of Neodymium Nitrate in Aqueous Solution

% $Nd(NO_3)_3$ by weight	Normality	Temp., °C.	Density	Refr. index 6563 Å.	Mol. volume	Mol. refraction
11.92	1.197	24.6	1.1054	1.34858	59.88	36.07
19.14	2.050	24.8	1.1792	1.35966	64.71	36 07
26.50	3.046	24.3	1.2652	1.37268	67.24	36.09
34.49	4.292	24.2	1.3698	1.38800	70.76	36.10
38.56	5.006	25.2	1.4290	1.39637	72.35	36.04
42.95	5 825	25.2	1.4930	1.40530	75.79	36.21
48.32	6.965	25.7	1.5867	1.41812	77.23	36.02
52.76	7.966	25.8	1.6620	1.42815	80.80	36.19
58.02	9.279	26.0	1.7604	1.44115	84.44	36.33
60.10	9.820	25.8	1.7986	1.44604	86.36	36.34

Table II

Molecular Volume and Refraction of Neodymium Chloride in Aqueous Solution

% $NdCl_3$ by weight	Normality	Temp., °C.	Density	Refr. index 6563 Å.	Mol. volume	Mol. refraction
13.46	1.830	26.6	1.1357	1.35898	23.49	29.93
20.40	2.978	26.9	1.2198	1.37570	26.51	30.07
25.37	3.914	27.0	1.2890	1.38922	28.01	29.91
30.53	4.993	2 7 6	1.3664	1.40356	29.23	29.65
35.01	6.031	2 7 8	1.4393	141724	31.22	29.58
38.18	6.855	24.6	1.5001	1.42873	31.26	29.40
44.84	8.739	25.2	1.6283	1.45228	34.69	29.33
47.55	9.639	25.0	1.6936	1.46360	34.72	29.03

ness the values previously reported for the perchlorate are included. While the perchlorate showed a 2% increase with concentration from 0 to 7 *N*, the nitrate shows a 1% increase from 0 to 10 *N*, and the chloride shows nearly a 3% decrease from 0 to 10 N. Over the same ranges of concentration the molecular volumes of these salts show a marked increase, the perchlorate 12%, the nitrate 27% and the chloride 36%.

In general the absorption bands of the neodymium solutions were shifted toward the red end of the spectrum by increasing concentration. In the case of the perchlorate the shifts were small, in most instances of the order of 1 or 2 Å., while both nitrate and chloride concentrated solutions showed marked shifts toward the red, those of the latter salt sometimes approach-

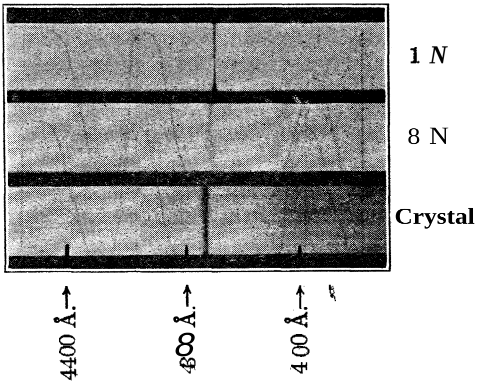


Fig. 2.—The 4272 Å. absorption line of neodymium nitrate.

ing 20 Å. The spectra of the dilute solutions of all the salts were practically identical.

As indicated in Figs. 2 and 3, the spectrum of the neodymium nitrate crystal showed a markedly increased shift in the same sense as did that of

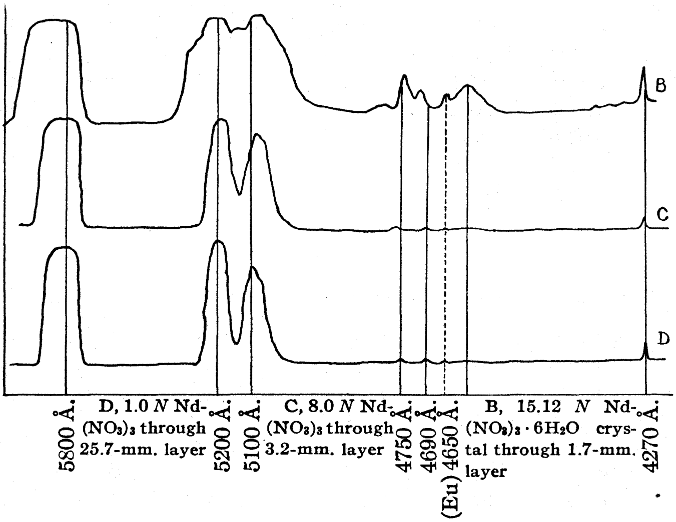
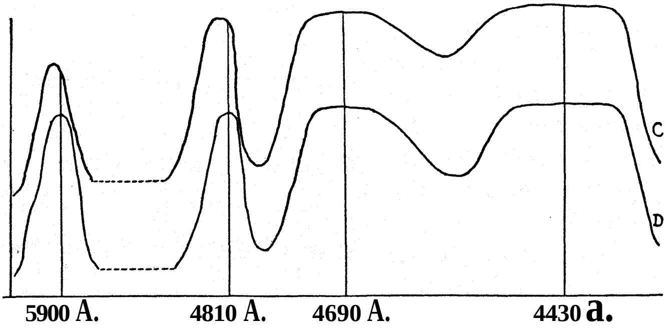


Fig. 3.—Microphotometric curves of the absorption spectrum of neodymium nitrate, showing the effect of concentration on the positions of the various bands.

the more concentrated solution. It is evident that whatever forces were causing the shifts in the solution were acting more intensely in the crystal.



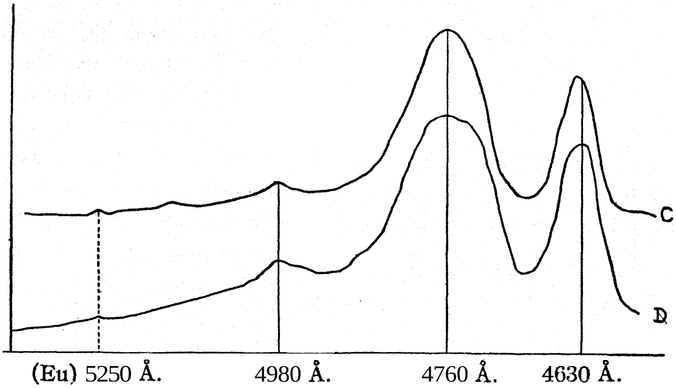
D, 0.2 N Pr$(NO_3)_3$ through 150-mm. layer; C, 10.0 *N* Pr$(NO_3)_3$ through 3-mm. layer.

Fig. 4.—Part of the absorption spectrum of praseodymium nitrate.

This observation parallels that of **Brunetti,**[4] who reached the same conclusion in the case of praseodymium salts.

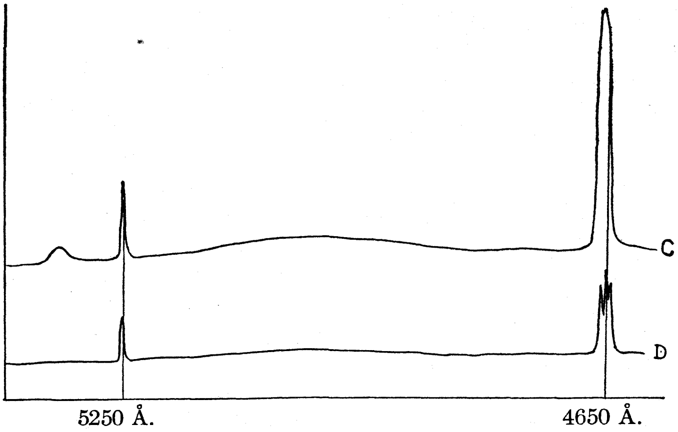
[4] Brunetti, *Nuovo cimento,* [N. S.] **5,** 391 (1928).

The spectral bands of praseodymium, samarium and europium also tended to shift toward the red with increasing concentration. The nitrate was investigated in every case. The bands of praseodymium were all shifted slightly toward the red, those of samarium were very slightly if at all shifted except the broad band at 4020 Å., which was noticeably moved toward the red. All the visible bands of europium seemed to be very slightly shifted toward the red. The relative intensities were also much changed. A few bands in the ultraviolet were too hazy to make any definite statement about their positions.



D, 0.2 *N* $Sm(NO_3)_3$ through 150-mm. layer; C, 10.0 N $Sm(NO_3)_3$ through 3-mm. layer.

Fig. 5.—Part of the absorption spectrum of samarium nitrate.

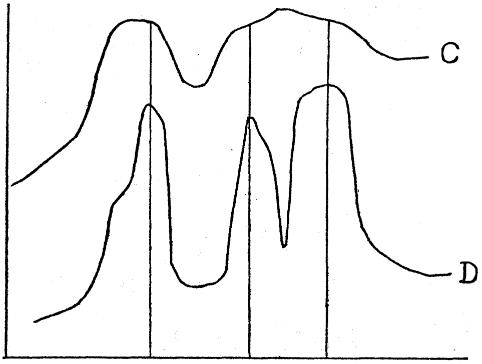


D, 0.2 *N* $Eu(NO_3)_3$ through 150-mm. layer; C, 10.0 N $Eu(NO_3)_3$ through 3-mm. layer.

Fig. 6.—Part of the absorption spectrum of europium nitrate.

At the concentrations employed no bands of gadolinium were observed at

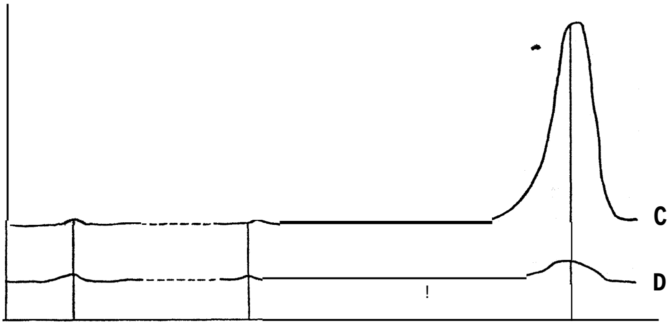
3108, 3059, 3056 or 3052 Å.,[5] where they have previously been reported. Several bands reported by Freed and Spedding, however, were found. Of these, the two at 2730 and 2750 Å. were most intense in the cases of both nitrate and chloride. While the nature of the bands was altered by concentration, it is doubtful whether there was any definite movement one way or another.



D, 0.2 *N* $GdCl_3$ through 150-mm. layer; C, 10.0 N $GdCl_3$ through 3-mm. layer.

Fig. 7.—Absorption bands of gadolinium chloride.

The bands, however, of holmium and erbium were generally shifted toward the blue, the change being most noticeable for those at 4530, 4850 and 5350 Å. for holmium, and 4430, 4490 and 6520 Å. for erbium. This peculiar change is so striking as to suggest some radical difference in the atomic structure of these last rare earth elements. Such a change is, in fact, postulated in the current theories of atomic structure, inasmuch as the 4_4 electron shell is believed to complete its first sextet with europium.[6] But the interpretation of the phenomenon is not entirely clear and it seems at the present time to be impossible to generalize further with respect to the effect of increasing concentration so far as direction of shift is concerned.



D, 0.2 N $Ho(NO_3)_3$ through 150-mm. layer; C, 10.0 N, $Ho(NO_3)_3$ through 3-mm. layer.

Fig. 8.—Part of the absorption spectrum of holmium nitrate.

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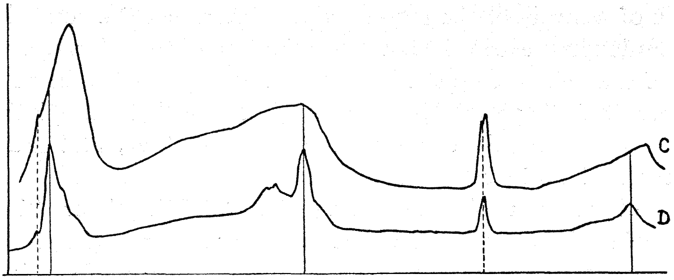
[5] Little, "A Textbook of Inorganic Chemistry" (Friend), London, Vol. IV, 1921, p. 289.

[6] Hevesy, "Die seltenen Erden von Standpunkte des Atombaues," Springer, Berlin, 1927.

As pointed out before, the classical dispersion formula shows that a decrease in characteristic frequency (shift toward the red) should be attended with an increase of molecular refraction. Such is what has been observed for the cases of neodymium perchlorate and nitrate.

Fajans and others have shown that while the perchlorate ion is only slightly influenced by its neighbors, the nitrate ion is somewhat deformed and the chloride ion is very highly deformed. While deformation of *a* cation results in an increase of refraction, deformation of an anion results in a decrease of refraction. It appears then that the increase in refraction of the neodymium ion is partly compensated by the decrease of the nitrate, and it is completely so and more by that of the chloride. The decrease in refraction of neodymium chloride is, therefore, in no way evidence against the conclusion that a shift toward the red of absorption bands is generally attended with an increase of refraction. It appears, then, from both refraction and spectroscopic evidence that the outer electron shell of the neodymium ion must be deformed in concentrated solution, and that this deformation is communicated in part, at least, to the inner electron shells thought to be the source of the characteristic absorption bands,



D, 0.2 N $Er(NO_3)_3$ through 150-mm. layer; *C*, 10.0 *N* $Er(NO_3)_3$ through 3-mm. layer.

Fig. 9.—Part of the absorption spectrum of erbium nitrate.

The writer wishes to thank Professor B. Smith Hopkins, in whose laboratory this work was done, for the invaluable advice and encouragement which he has from time to time supplied.

Summary

The molecular refraction of neodymium nitrate has been found to increase slightly with concentration, while that of the chloride decreases. The molecular volume of both salts is increased. The absorption bands are shifted toward the red. These measurements afford evidence that the neodymium ion is deformed in the more concentrated solutions. The absorption bands of praseodymium and samarium nitrates are also shifted toward the red. The bands of europium and gadolinium are not much

altered in position, while those of holmium and erbium are noticeably shifted toward the blue.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CHICAGO]

STUDIES ON COMPLEX IONS. III.[1] THE RELATIVE STABILITIES OF THE HALOGENOPLATINATES

BY H. I. SCHLESINGER AND R. E. PALMATEER[2]

RECEIVED AUGUST 30, 1930 PUBLISHED NOVEMBER 5, 1930

As part of a study of the factors which determine the conditions under which complex ions are formed, a determination of the relative stabilities in solution of a series of complex ions of similar types has become desirable. Schlesinger and Tapley[3] have shown that the halogenoplatinates are mutually and reversibly convertible into each other, and are therefore suitable for such an investigation.

The usual method of determining the "stability" or "instability" constants of such ions is inapplicable to this case, for aqueous solutions of the halogenoplatinates contain no detectable quantities of the free platinic ions. Relative values of the stabilities might, however, be obtained if the amount of transformation of one halogenoplatinate into the other could be determined in the presence of given quantities of halide ions. But even such measurements present difficulties, for the reactions involved probably proceed in many steps, leading through all of the theoretically possible mixed halogenoplatinates. No method available allows a determination of each of the seven possible components of such a system.

It nevertheless has become possible to obtain approximate relative values by the following procedure. When, for example, a chloroplatinate is mixed in aqueous solution with a bromide and a chloride in suitable proportions, a reaction occurs which leads to the formation of a mixture intermediate in color between that of the pure chloroplatinate and the pure bromoplatinate. An identical mixture, at least so far as the color is concerned, is obtained if the starting material is the bromoplatinate, a fact which demonstrates that a state of true equilibrium is attained. By comparing photometrically the color of such solutions with mixtures of chloro and bromoplatinates of known concentration, one could estimate the percentage of transformation of the one platinate into the other were no

[1] For the preceding papers of this series see THIS JOURNAL, 51, 3520, 3523 (1929).

[2] This paper is taken from a thesis presented by R. E. Palmateer to the Faculty of the Ogden Graduate School of Sciences of the University of Chicago, in part fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Schlesinger and Tapley, THIS JOURNAL, 46, 276 (1924).

intermediate chloro-bromoplatinates formed. From this percentage transformation one could then calculate the ratio of the concentrations of the two complex ions. But, as will be demonstrated in the experimental part of this paper, intermediate complex ions are undoubtedly present, and the color of the solutions is, on that account, not a direct measure of the percentage transformation nor of the ratio of the concentrations of the complex ions. However, as the calculated ratios approach zero or infinity the fictitious values must approach the true ratio. That this assumption is warranted is shown by the fact that under these conditions the colors, as well as the absorption spectra, approach those of the pure complex ions. Hence, by plotting the values of these fictitious ratios[4] against the ratios of the concentrations of the simple halide ions involved in the reaction, and extrapolating the curves to a point representing practically complete transformation, one can determine at what concentrations of the simple ions the transformation of the one complex ion into the other becomes complete. The extrapolation proved to be unexpectedly reliable because the curves proved to be straight lines.

Ratios of the simple ions found in this way to be necessary almost completely to transform one of the halogenoplatinates into the other are very striking. To convert 99% of bromoplatinate[5] into chloroplatinate, the solution must contain approximately 660 times as much sodium chloride as sodium bromide, and to produce the corresponding result in the reaction between iodoplatinate and bromoplatinate, there must be present approximately 25,000 times as much sodium bromide as sodium iodide. From these data we have estimated, by a method to be described below, that to convert iodoplatinate ions almost completely into chloroplatinate ions, the solution must be approximately 16,600,000 times as concentrated

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[4] These fictitious ratios, calculated from the colorimetric data, will hereafter be called the "apparent ratios" and the corresponding percentage transformation will be called the "apparent % transformation" and will be designated by the letter P.

[5] The choice of 99% for the calculation was based on the following reasons. Theoretically, 100% conversion cannot occur until the concentration of one of the simple halide ions reaches infinity. The data obtained could have been used to calculate the ratio of the simple ions required to produce any degree of transformation below 100%, but such calculations have a concrete meaning only for almost complete transformation, because only under that condition is the color a measure of the amount transformed. Another point of importance should be noted at this time. While it is undoubtedly true that the "apparent ratios" (see footnote 4) approach the true ratios, the two values might still be fairly widely different even at 99% transformation; but that is of no significance. In the transformation of bromoplatinate into chloroplatinate, for example, the color of the solutions is practically identical with that of the latter substance when the "apparent ratio" is 99:1. Hence practically all of the material is in the form of chloroplatinate. The remaining 1% may be largely an intermediate ion instead of bromoplatinate. Consequently the true ratio may be far from 99; but 99% of the material is nevertheless in the form of the chloroplatinate, and this is the quantity in which we are interested.

with respect to sodium chloride as to sodium iodide. An attempt was made to determine the corresponding quantities for the equilibrium between fluoroplatinate[3] and iodoplatinate. The reaction requires months for completion at ordinary temperatures, and the solutions attack glass vessels and undergo decomposition. For these reasons no reliable data have been obtained, but the results indicate that the great difficulty of transforming fluoroplatinate into the other ions is possibly due in part to the sluggishness of reaction rather than entirely to inherent stability.

It is interesting to point out that the results here reported demonstrate how enormously greater is the tendency of iodide ion than of bromide ion, and of bromide ion than of chloride ion, to enter the coordination sphere in the case of the platinates. In the case of some of the solid ammines of chromium and certain other metals, according to the data obtained in this Laboratory and elsewhere,[6] the reverse is true. Whether the difference is to be explained by the influence of changes in lattice energies in reactions between solid compounds as has been suggested,[6] or is to be accounted for by specific influences of the central atoms, can be decided only when further data have been collected. The most likely cause for the difference, however, would seem to be that, in the platinates, the halogen ions are contained in a negative complex ion, while in the other compounds mentioned they are in a positive complex ion.

In the course of this investigation we have had occasion to review the evidence on which rests the idea that all possible intermediate halogenoplatinate complexes exist, and to contribute further data along these lines. We have made some interesting observations on the rates at which equilibria in such mixtures are established, as well as on some other properties of the halogenoplatinates. These observations as well as additional phases of the interpretation of our data will be taken up below.

Experimental

Preparation of Materials.—The platinum from which the salts were prepared was purified by recrystallizing sodium chloroplatinate from alcohol and further by the procedure of Mylius and Mazzucchelli.[7] From the platinum thus purified sodium chloroplatinate was prepared according to the method of Precht.[8]

Potassium bromoplatinate was obtained according to the procedure of Biilmann and Andersen[9] and further purified by two recrystallizations, which yielded a product of constant absorption spectrum. The corresponding sodium salt was obtained by adding a dilute solution of sodium bicarbonate to bromoplatinic acid, an intermediate product in the preparation of the potassium salt. The solution was evaporated to a sirupy consistency on a water-bath and dried in a vacuum desiccator over phosphorus pentox-

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[6] See Ref. 1 and Biltz, *Z. anorg. allgem. Chem.*, 130, 93 (1923); 166, 351 (1927). Other references will be found in the articles cited.

[7] Mylius and Mazzucchelli, *Z. anorg. Chem.*, 89, 1 (1914).

[8] Precht, *Z. anal. Chem.*, 18, 509 (1879).

[9] Biilmann and Andersen, *Ber.*, 36, 1565 (1903).

ide. The resulting solid was dissolved in absolute alcohol, the solution filtered and treated with ether to precipitate the sodium bromoplatinate.[10] Von Bonsdorff[11] claims to have prepared sodium bromoplatinate bv the addition of sodium bromide to bromoplatinic acid; but sodium bromide is less soluble in water or in alcohol than is sodium bromoplatinate, and his method therefore leads to no results.

Datta's[12] method for the preparation of potassium iodoplatinate was used, and that of Schlesinger and Tapley[a] for the potassium flnoroplatinate. In the latter case it was found preferable to heat the mixture of platinum and the double salt of lead tetrafluoride to just below the melting point of the latter, because under these conditions a better yield was obtained than that described in the earlier paper.

Sodium chloride and sodium iodide were purified by repeated recrystallization from commercial salts of good quality. The iodide was shown by the usual methods to be free from chloride. Sodium bromide was prepared from repeatedly redistilled hydrobromic acid and sodium bicarbonate. The final product contained too small a quantity of sodium chloride to be detected by the ordinary methods of titration. Sodium fluoride was prepared similarly from hydrofluoric acid. The usual drying of these salts by heating them to redness in platinum vessels was omitted, as it was shown spectroscopically that such a procedure introduced traces of the corresponding platinates.[13]

The measurement of the "apparent % transformation" could not be made by a direct comparison of the color of the unknown solutions with that of solutions containing known amounts of the halogenoplatinates in question, because synthetic mixtures cannot be prepared. Both bromo and iodoplatinates undergo moderately rapid decomposition in pure water. To stabilize the former a soluble bromide and for the latter an iodide must be added to the solutions. If these stabilizing salts were added to a mixture of these two platinates or to a mixture of either of them with a chloroplatinate, partial transformation to the more stable complex ion would occur.

It was, therefore, necessary to calculate from the color intensity of the separate halogenoplatinates what must be the color intensity of mixtures of the two salts. To do this we first proved both colorimetrically and spectrophotometrically that each of the salts obeyed Beer's law. Next it was found, for example, that a column of 0.0016 molar sodium chloroplatinate 50 mm. long matched the color of a 3-mm. column of 0.0016 molar sodium bromoplatinate[14] in a Kober colorimeter. Consequently if $P\%$ of the chloroplatinate in the first solution were transformed to bromoplatinate, a column H mm. in length would have to be used to match a 10-mm. column of the 0.0016 molar standard bromoplatinate solution when

[10] This salt is so hygroscopic that we did not weigh it out in making up the standard solutions, but determined the strength of the solution prepared by colorimetric comparison with a standard solution of the potassium salt.

[11] Von Bonsdorff, ***Pogg. Ann.***, 19,344 (1830); 33, 61 (1834).

[12] Datta, THIS JOURNAL, **35**, 1186 (1913).

[13] The amount of platinate was less than 0.00002 molar in the saturated solutions of the simple salts, but was easily discernible in the spectra.

[14] The standard solutions of this salt always contained sufficient sodium bromide to prevent hydrolysis.

$$H = \frac{1000}{P + \frac{3}{50}(100 - P)}$$

The values of P in this equation are what have been called the "apparent % transformation" in the preceding discussion.[4] For the reaction between bromo and iodoplatinates a similar procedure was used, except that the color of the mixtures was compared with that of a 0.0001 molar iodoplatinate solution stabilized by sodium iodide. The equation for calculating the percentage transformation, obtained as described for the preceding case, was

$$H = \frac{1000}{P + \frac{208}{50}(100 - P)}$$

Although this method gives fairly satisfactory results, it suffers from the difficulty that, in spite of the fact that dilute solutions of these various platinum salts are similar in color, the shades are not exactly alike. For this reason colorimetric readings are difficult to duplicate for a given mixture more closely than to 1% in the most favorable case, that is, when the apparent transformation is about 50%, and to 7% in the least favorable cases, that is, when the reaction has gone nearly to completion toward the formation of the less intensely colored compound. Ten to fifteen readings were therefore made of each solution, and all the solutions were made up in several portions. Consequently each of the "apparent % transformations" tabulated below is really the average of from thirty to sixty readings. Since the errors are less marked in dilute than in concentrated solutions, the former were used exclusively. Finally, measurements were restricted to solutions of from three to five different concentrations of the platinum salts, because for each concentration the constants for the equations given above had to be redetermined.

It might be expected that provision would have to be made for keeping the mixtures at constant temperature both while equilibrium is being reached and during the measurement of the color, but this was found to be unnecessary for the degree of precision to which we were limited by the sources of error described. Thus we observed that even though the solutions were kept in the colorimeter for from ten to twenty minutes for measurement, there occurred no change in the reading greater than the reading error itself. Unquestionably this is in part due to the slowness of the transformation of bromoplatinate into chloroplatinate and vice *versa,* but the lack of disturbance caused by temperature changes must be largely due to a very small temperature coefficient for the equilibrium condition. This is shown by two facts. In the first place, the data obtained from solutions kept at 25° in a thermostat did not differ from data on solutions kept in the room. In the second place, the colors of the equilibrium mixtures for the transformation of iodoplatinate into bromoplatinate also remained constant in the colorimeter although in this case equilibrium is attained in a few minutes.

Rate of attainment of equilibrium is greatly affected by light. The reaction between a bromoplatinate and a chloride in a mixture exposed to the light of a north window came to completion in three days; another portion of the same solution was kept in a thermostat in a blackened flask, and did not reach equilibrium before the fiftieth day. Nevertheless, the final equilibrium reading was the same in the two cases. Consequently there is a great advantage in keeping the mixtures exposed to light instead of in a constant temperature bath, and the data presented below, therefore, refer to the reaction at room temperature, *i. e.*, from 20–25°.

In Table I are given the experimental results for the equilibrium between chloroplatinate and bromoplatinate ions. The first column gives the initial concentration of the platinates in moles per liter. The subscript B indicates that equilibrium was reached from the bromoplatinate, the subscript C that the equilibrium was reached from the chloroplatinate side of the reaction. The second and third columns give, respectively, the initial concentrations of the sodium chloride and the sodium bromide in moles per liter. The length of column of the equilibrium mixture required for a color match when read against a 10-mm. column of a solution of potassium bromoplatinate of the same concentration as that of the platinate in the original solution is given in the fourth column.[15] The fifth column is the "apparent % transformation" of chloroplatinate into bromoplatinate, defined and obtained as has already been described. Obviously the transformation of the one halogenoplatinate into the other must be accompanied by decrease in the concentration of one of the simple halide ions and a corresponding increase in the other. Hence the equilibrium ratio of the simple halides differs from the ratio of the initial concentrations. To calculate the former we again proceeded as if no intermediate platinate ions were formed. Consequently these ratios are also fictitious, but they, too, must approach the real values as the "apparent % transformation" approaches 100. In fact, in most of the experiments the change in the ratio of the simple salts resulting from transformation of the platinates is very small, since a large excess of the simple ions was usually present. The calculation of the equilibrium ratios from the "apparent % transformations" is thus made on the basis of the chemical change represented by the equation

$$6\mathrm{NaY} + \mathrm{Na_2PtX_6} \rightleftharpoons 6\mathrm{NaX} + \mathrm{Na_2PtY_6}$$

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[15] Potassium bromoplatinate was used as a standard because it can be weighed out accurately while the sodium salt is too hygroscopic; but in the equilibrium mixtures the sodium salts had to be used because potassium chloroplatinate would be precipitated from the solution and the equilibrium, therefore, disturbed.

in which X and Y represent halide ions. In Col. 6 are given the equilibrium ratios of the halide ions, and in Col. 7 the corresponding ratios for the platinate ions. As was pointed out above, when these ratios are plotted against each other, a straight line results. Hence, the product of the one set of ratios by the reciprocal of the other is a constant, the value of which is shown in Col. 8.

TABLE I

EXPERIMENTAL DATA

Halogeno-platinate	Sodium chloride	Sodium bromide	Reading, H	% Trans-formation, P[a]	Equilibrium ratios		Const.
					NaBr/NaCl	$PtBr_6/PtCl_6$	
0.0016_C	1.3	0.034	54.4	13.37	0.02513	0.154	0.163
$.0016_C$	1.1	.0325	50.18	15.25	.02814	.18	.156
$.0016_C$	0.9	.027	48.8	36.00	.02817	.19	.148
$.0016_C$	1.0	.033	46.3	17.12	.03125	.208	.155
$.0016_C$	1.1	.039	45.87	17.25	.03387	.212	.159
$.0016_C$	1.0	.0385	45.3	17.75	.03674	.214	.171
$.0016_C$	1.3	.051	42.5	19.4	.03775	.24	.157
$.0016_C$	0.85	.0374	40.83	20.4	.0416	.256	.162
$.0016_C$	1.0	.044	36.98	23.08	.0417	.2975	.140
$.0016_C$	1.0	.044	40.9	**20.42**	.04196	.256	.164
$.0016_C$	0.65	.03575	34.87	24.4	.05109	.318	.161
$.0016_C$	1.0	.055	32.52	26.42	.0522	.356	.146
$.0016_C$	1.0	.055	34.7	24.5	.0525	.329	.159
$.0016_C$	1.0	.055	34.8	24.4	.05254	.32	.161
$.0020_C$	0.95	.055	25.97	26.0	.0544	.358	.152
$.0017977_B$	1.0	.05	26.41	29.46	.0581	.418	.139
$.0017977_B$	1.0	.055	25.82	30.29	.063	.433	.145
$.0016_C$	0.55	.0385	30.63	28.12	.06477	.391	.165
$.0016_C$	.7	.05	30.17	28.7	.0672	.404	.166
$.0016_B$	.85	.05	30.19	28.7	.0674	.404	.167
$.001387_B$	.7	.05	30.32	32.6	.080	.4849	.165
$.0016_C$	1.0	.088	24.43	37.98	.084	.606	.138
$.0020_C$	0.55	.055	19.7	36.75	.091	.588	.155
$.0016_C$	.5	.05	22.55	41.4	.0915	.695	.133
$.0016_C$	.55	.055	24.6	36.75	.09299	.586	.158
$.0017977_B$	1.0	.088	19.36	33.75	.0949	.739	.128
$.0017977_B$	1.0	.1	18.9	43.7	.1072	.777	.138
$.0016_C$	0.55	.066	21.41	43.375	.1115	.77	.144
$.00177_B$	.45	.05	18.21	46.6	.125	.872	.143
$.0020_C$	.45	.0675	15.98	47.0	.1358	.877	.154
$.0016_C$	.45	.0675	18.56	50.75	.1408	1.04	.136
$.0016_C$	.45	.0675	18.71	50.5	.1410	1.01	.140
$.0016_C$	.43	.07	19.42	48.5	.1505	0.942	.159
$.0016_C$	.41	.0738	17.61	54.0	.1602	1.18	.140
$.00177_B$	.43	.07	15.83	54.4	.176	1.18	.149
$.0020_C$	.41	.082	13.85	55.00	.181	1.22	.141
$.0016_C$	.41	.082	16.77	57.5	.18413	1.34	.137
$.0016_C$	.41	.082	1684	57.0	.18416	1.32	.140
$.0016_C$	.33	.0762	16.3	59.0	.1993	1.44	.138
$.00177_B$	.415	.085	14.64	59.4	.2175	1.485	.149

TABLE I *(Concluded)*

Halogeno-platinate	Sodium ctrloride	Sodium bromide	Reading, *H*	% Transformation, P[a]	Equilibrium ratios NaBr/NaCl	Equilibrium ratios $PtBr_6/PtCl_6$	Const.
0.0016_C	0.33	0.0825	15.76	61.2	0.228	1.58	0.144
$.0016_C$	.4	.1	16.75	57.2	.233	1 345	.173
$.00177_B$	.4	.1	13.55	64.2	.262	1.807	.145
$.0020_C$	.25	.075	12.2	63.5	.2626	1.74	.151
$.0016_C$	.25	.075	14.66	65.5	.2679	1.94	.138
$.0016_C$	.23	.07	14.7	65.5	.269	1.91	.141
$.0016_C$	.25	.0875	14.13	68.5	.3153	2.2	.141
$.0016_B$	.16	.05	15.16	650	.341	1.85	.184
$.001387_B$	.37	.13	15.4	71.9	.36	2.555	.141
$.0016_C$	1.00	.375	13.44	72.95	.366	2.635	.138
$.0016_C$	0.35	.15	13.36	73.0	.401	2.735	.146
$.0016_C$	.2	.1	12.78	77.0	.446	3.35	.133
$.0016_C$	.5	.25	12.9	76.47	.478	3.163	.151
$.0016_C$	.32	.18	13.06	75.2	.527	3.2	.165
$.0016_C$	.2	.15	12.32	80.0	.686	4.00	.171
$.0017977_B$	.5	.375	10.46	85.08	.756	5.3	.142
$.0017977_B$	.25	.25	10.21	86.39	1.01	6.4	.158

[a] It must be borne in mind that the equations given above for calculating "P" from "*H*" merely show the principles employed. The solutions actually used as color standards did not always have exactly the same concentration as the experimental solutions, and the values of "P" in the table are corrected for this difference. Furthermore, "P" represents the fraction present as bromoplatinate irrespective of the side from which equilibrium was reached. Similar considerations apply to Table II.

It will be seen from the table that there are considerable deviations from the linear relationship between the "apparent % transformation" and the ratio of the concentrations of the simple halide ions. These deviations, however, show no trend, and can be fully accounted for by the unavoidable reading errors which have already been discussed. To show at a glance that the deviations are symmetrical throughout, we have reproduced the experimental results in Fig. 1. Instead of plotting the two ratios directly, we calculated from the constant what should be the curve for the plot of the "apparent" ratio of the concentration of complex ions against the logarithm of the "apparent' ratio of the concentrations of the simple ions. These curves are shown in solid lines; the circles representing the experimental data show no trend.

The data furthermore show that the equilibrium is determined by the ratio of the concentrations of the substances involved rather than by the values of the concentrations themselves. Thus, for example, there are two mixtures in which the apparent ratio of the concentrations of the sodium bromide to sodium chloride was 0.262 at equilibrium. Although one of these solutions contained 0.1038 mole of sodium bromide and 0.3962 mole of sodium chloride and the other 0.0674 mole of bromide and 0 2576 mole of the chloride. the constant for the first set of data is 0.145 and for the second set 0.151. The difference between the two values is accounted far by a reading error of 1%, which is well within the limit attainable in the experiments. These two solutions illustrate also that the changes in the concentration of the platinate are without effect on the constant, for the first solution was 0.00177 molar with respect to this constituent and the second 0.0020. It should be stated, however, that the platinate concentrations were not varied between wide limits for reasons discussed previously. Numerous other cases showing that the constant is independant of the initial concentrations will be found in the table.

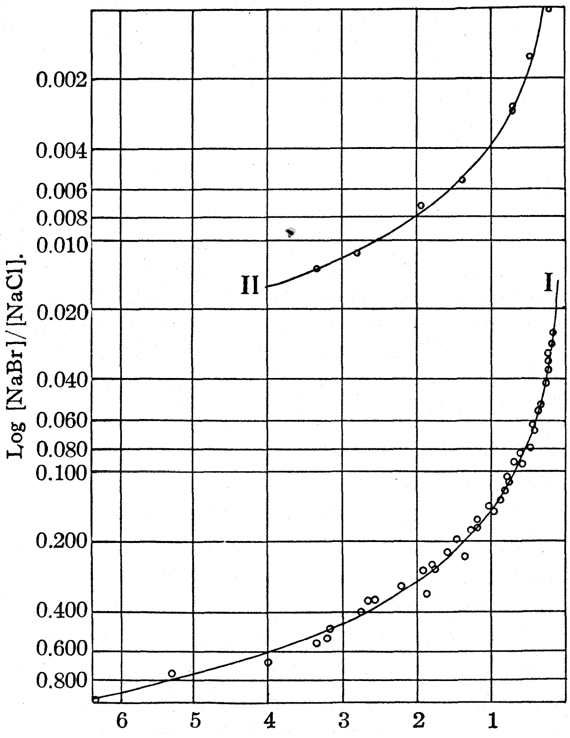

Fig. 1.—Curve I, $[Na_2PtBr_6]/[Na_2PtCl_6]$; Curve II, $[K_2PtI_6]/[K_2PtBr_6]$.

From the average value of this constant we may now calculate the conditions under which bromoplatinate is 99% transformed to chloroplatinate. For, as has already been said, as the "apparent % transformation" approaches 100% it also approaches the value of the real per cent. transformation. The equation by which the constants of Table I were calculated is

$$\frac{[NaBr]}{[NaCl]} \times \frac{[Na_2PtCl_6]}{[Na_2PtBr_6]} = 0.15$$

in which the bracketed symbols denote molar concentrations. If [NaBr] = 1, the ratio $[Na_2PtCl_6]/[Na_2PtBr_6]$ becomes 99 when [NaCl] = 660.

In Table II are given the corresponding data for the equilibrium between iodoplatinate and bromoplatinate ions. In addition to the difficulties of measurement mentioned above, another source of error proved troublesome in this case. Very small traces of alkali, even those dissolved from glass by the solutions, cause decomposition of the iodoplatinate. To prevent this, bromide ion was supplied in part in the form of hydrobromic acid. In these solutions, however, iodine is fairly rapidly liberated, probably on account of reduction of the platinum to the platinous condition since the reaction occurs in solutions free from oxygen. Fortunately the liberation of iodine is much slower than the attainment of the equilibrium under investigation, and causes no serious difficulty if the measurements are made rapidly. The great difference in speed of attainment of equilibrium in the reaction between chloro and bromoplatinate and in that between bromo and iodoplatinate is of considerable interest. For the present we can state, however, only that in the former case equilibrium was reached in about three days in daylight, while in the latter only thirty to eighty minutes are necessary.

TABLE II

EXPERIMENTAL DATA

Halogeno-platinate	Bromide concentration	Sodium iodide	Reading, H	% Transformation, P	Equilibrium ratio		Constant
					NaI/HBr	$PtI_6/PtBr_6$	
0.0001_I	0.8462	0.011	12.93	76.7	0.01318	3.29	0.00400
$.0001_B$	1.6924	.02	13.5	73.5	.01155	2.777	.00416
$.0001_I$	0.8462	.006	15.05	65.5	.00722	1.90	.0038
$.0001_B$	0.8462	.005	16.82	57.6	.0055	1.358	.00405
$.0001_B$	1.6924	.005	22.75	41.0	.00281	0.695	.00405
$.0001_I$	0.8462	.002	24.00	39.0	.00279	.639	.00436
$.0001_I$	.8462	.002	22.84	41.4	.00278	.707	.00393
$.0001_I$	.8462	.002	23.02	41.0	.00278	.695	.0040
$.0001_I$	.8462	.002	23.17	40.7	.00278	.686	.00405
$.0001_B$	.8462	.0025	23.24	40.5	.00266	.68	.00391
$.0001_I$	.8462	.001	29.82	30.6	.001643	.431	.00382
$.0001_B$	1.6924	.001	60.3	12.7	.000545	1.455	.00374

Again the values in Col, 8 are constant to well within the range of experimental error. Hence, when transformation is almost complete

$$\frac{[\mathrm{NaI}]}{[\mathrm{NaBr}]} \times \frac{[\mathrm{Na_2PtBr_6}]}{[\mathrm{Na_2PtI_6}]} = 0.004$$

Substituting 1 for [NaI], 99 for $[Na_2PtBr_6]/[Na_2PtI_6]$, [NaBr] becomes approximately 25,000.

If we multiply the equations $[NaI]/[NaBr]$ X $[Na_2PtBr_6]/[Na_2PtI_6] = 0.004$[16] and $[NaBr]/[NaCl] \times [Na_2PtCl_6]/[Na_0PtBr_6] = 0.15$ by each

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[16] The actual measurements for this equation were carried out with solutions containing hydrobromic acid and sodium bromide for the reasons given above, but for the very rough calculations now to be discussed, substitution of the salt for the acid will make no difference. As a matter of fact, we showed experimentally that the same value for this constant would have been obtained had sodium bromide alone been used.

other we obtain

$$\frac{[\mathrm{NaI}]}{[\mathrm{NaCl}]} \times \frac{[\mathrm{Na_2PtCl_6}]}{[\mathrm{Na_2PtI_6}]} = 0.0006$$

This is admittedly a mathematical procedure of very uncertain justification. In obtaining the constant values 0.004 and 0.15, we substituted in the first two equations numerical values which in all probability represent concentrations only under the very definite conditions specified above. There was no well-established theoretical basis for expecting that the products of these ratios would be constants, and there is, therefore, no reason for anticipating that a similar relationship would prove true in the case of the equilibrium between iodoplatinate and chloroplatinate, but the last-named equilibrium cannot be studied in the same way as were the others, because the colors obtained, when attempts were made to cause partial transformation, are not intermediate in shade between those of the iodo and chloroplatinate. This is not surprising, for iodoplatinates differ very markedly in color from the chloroplatinates, and if intermediate compounds exist there should be a variety of shades in the equilibrium mixtures. For this reason it was necessary to find a way of estimating mathematically under what conditions almost complete transformation should occur, and then to corroborate this estimate approximately by experiment. The derived equation seemed the most rational approach to the solution of the problem.

According to this equation it would be impossible to transform more than a small fraction of iodoplatinate into chloroplatinate by the addition of chloride ion. A minimum of 0.001 molar potassium or sodium iodide is required to prevent decomposition of iodoplatinates into platinum tetraiodide. If this amount of potassium iodide is present in the solution, the equation requires that the concentration of the chloride ion constituent would have to be 16,000 normal for 99% transformation. In accordance with this prediction, it was found that iodoplatinates, stabiliied with a minimum amount of potassium iodide and treated with a large excess of 6 molar hydrochloric acid, retain a much more intense color than they should, had the iodoplatinate been completely changed to chloroplatinate.[17]

Somewhat more definite information can be obtained by studying qualitatively the reverse reaction. According to the equation it is necessary to make the concentration of the chloride approximately 0.2 molar in order to prevent practically complete transformation of chloroplatinate to iodoplatinate when the former is dissolved in 0.001 molar potassium iodide. A solution thus prepared, using 0.0001 molar sodium chloroplatinate, does

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but since decomposition tended to occur under these conditions the data were not as reliable as those obtained with the acid.

[17] If concentrated hydrochloric acid is used, the color of the solution gradually fades. The absorption spectrum of this solution shows, however, that the iodoplatinate has been transformed into compounds other than chloroplatinate. Also the addition of potassium iodide to these solutions does not completely reverse the reaction.

not quite attain the color of iodoplatinate of this concentration, but the experiment is only of qualitative character because decomposition to platinum tetraiodide cannot be entirely prevented. On the other hand, a solution molar with respect to hydrochloric acid, 0.001 molar with respect to potassium iodide and 0.0001 molar with respect to sodium chloroplatinate showed, when equilibrium was reached, the brown color characteristic of partial transformation instead of the violet shade of the iodoplatinate. Obviously, then, the data calculated from the derived equation do give results correct at least so far as the order of magnitude is concerned.

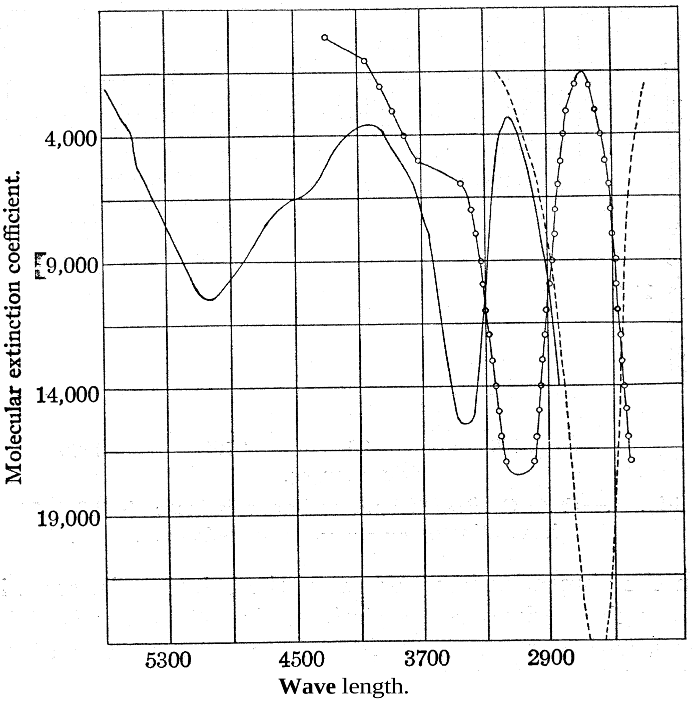

Fig. 2.— - - - -, K_2PtCl_6; O-O-O, K_2PtBr_6; ——, K_2PtI_6.

There are several points of theoretical interest which should be indicated, although our data are as yet too limited to warrant extended discussion. One would expect that equilibrium conditions in the reactions investigated would be expressed by equations of the type $[PtX_6^=][Y^-]^6/[PtY_6^=][X^-]^6 = K$; instead, an equation in which the apparent concentrations of the simple halogenide ions appear as the first power results from the data. The lack of agreement with the mass law is not surprising. We have neglected the activity coefficients; in dilute solutions these might cancel out because of the great similarity of the pairs of ions involved, but in the concentrations used this is hardly to be expected. But the most probable reason for the enormous deviation from the mass law is the possibility that the apparent concentrations are in most instances not the real concentrations because of the formation of intermediate complex ions. Since the existence of such substances has repeatedly been denied, further investigation of this point was undertaken as described below.

While it is thus not difficult to explain the deviation from the mass law, no satisfactory explanation has as yet been found for the fact that the "apparent ratios" happen to vary with the first power of the ratio of the concentrations of the halogenide ions. A possible explanation is that the change in the absorption band, as one of the halogenoplatinates is transformed through a series of mixed platinates into the other, is divided into equal steps, and that the distribution of the concentrations of all of the complex ions is a symmetrical one. Since six such steps are involved in the "apparent % transformation," one might obtain the relationship

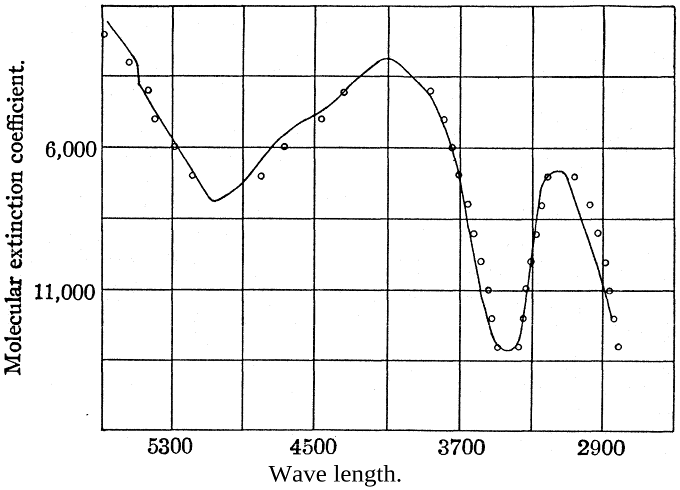

Fig. 3.—○ ○ ○, 0.000025 molar bromoplatinate + 0.000075 iodoplatinate; ———, calculated curve.

(Apparent ratio of complex ions) ▾ ▾ (apparent ratio of simple ions)^6 = constant

This, of course, is what we have found. We believe, however, that too many assumptions are involved in this idea to warrant its acceptance on the basis of the one set of data thus far obtained; the first power relationship may, indeed, be purely accidental.[18]

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[18] It is also possible that the first power relationship means that the color change is complete in the first step of the series of reactions, for example, that the color of the hypothetical $PtCl_5Br^=$ ion is identical with that of the $PtBr_6^=$ ion. This explanation does not fit with the fact that the values for the constant are independent of the side from which equilibrium is attained nor with facts presented in the following section of this paper.

Existence of Mixed Halogenoplatinates

The existence of the mixed halogenoplatinates has been affirmed and denied. Pitkin[19] and Pigeon,[20] by crystallization of mixtures of chloro- and bromoplatinates, claimed to have obtained mixed chlorobromoplatinates. The former also reported the preparation of the compound $K_2PtCl_4Br_2$ by the action of potassium bromide on platinic chloride. Herty[21] demonstrated that none of these substances was a true compound, and Miolati,[22] by conductivity methods applied to solutions, likewise concluded that there is no evidence for formation of mixed compounds.

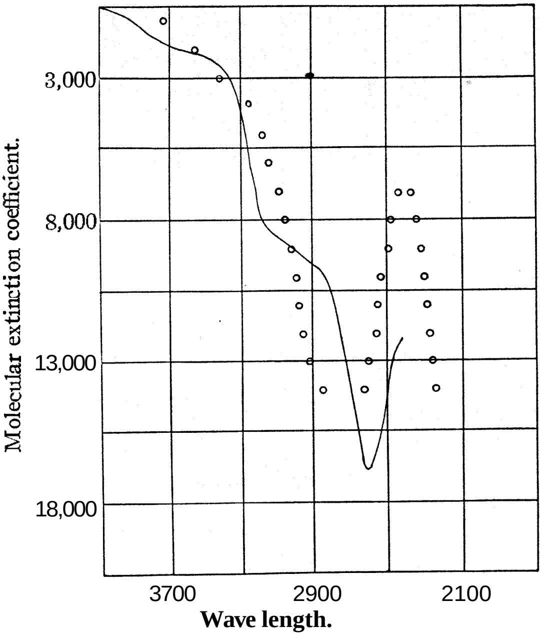

Fig. 4.—O O O, equilibrium mixture—colorimetrically 39.2% $PtBr_6$ and 61.8% $PtCl_6$; ————, calculated curve.

The experimental work herein reported makes possible another method of attacking this problem. If the mixtures prepared by adding, for example, sodium bromide to sodium chloroplatinate contain no intermediate complex ions, the value of the "apparent % transformation" obtained colorimetrically is the real percentage transformation. From the latter we could then calculate the amount of the chloroplatinate and the bromoplatinate in the solutions. With this information and with photometrically determined absorption spectra of each of the platinates, the position of the absorption band of the solution should be calculable.[23] If the calculated and the observed spectra coincide, no intermediate complexes are present. The curves to be presented below show that this is not the case.

Before proceding with these measurements, it seemed desirable to verify the method of calculating the spectra for the mixtures in question. As has

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[19] Pitkin, This Journal, 1,472 (1879); 2,408 (1880).

[20] Pigeon, *Ann. chim.*, [7] 2,488 (1894).

[21] Herty, This journal, **18,** 130 (1896).

[22] Miolati, *Z. anorg. Chem.*, 14,238 (1879).

[23] Kayser, "Handbuch der Spektroskopie," S. Hirzel, Leipzig, 1905, Vol. III, p. 92.

already been pointed out, mixtures of known quantities of the two halogenoplatinates cannot be prepared. Consequently we remodeled the Hilger sector photometer to permit us to insert two separate cells into each of the photometer tubes. This allowed **us** to have the'light fall first through a solution of chloroplatinate and then through one of the bromoplatinate before entering the spectrograph.

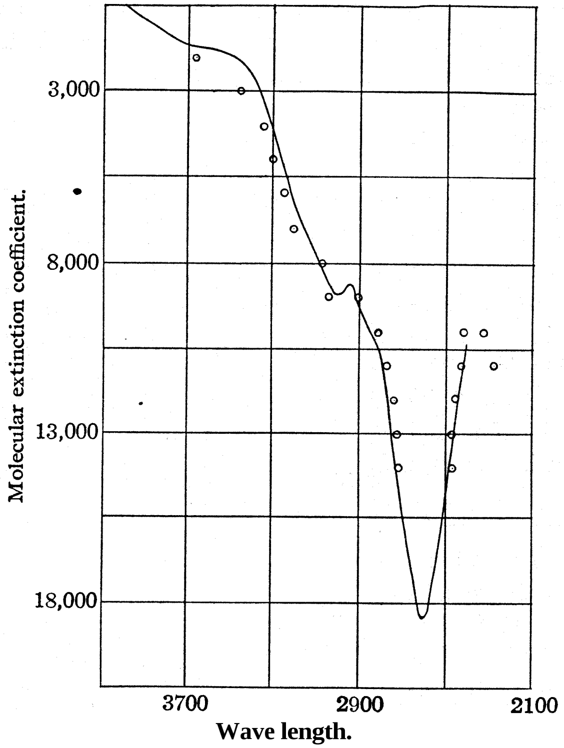

Fig. 5.—0 O 0.0.0001 **molar "$K_2PtCl_4Br_2$;" ———, calculated curve.**

In Fig. **3** the solid line represents the calculated molecular extinction coefficients for a mixture of chloroplatinate and bromoplatinate while the circles are values obtained in the way just described from the absorption spectra of the separate halogenoplatinates reproduced in Fig. 2. Similar curves for bromo and iodoplatinate were obtained but are not reproduced. The agreement is as good as can be expected, and proves that the usual method of calculating the extinction coefficient for solutions of mixtures is applicable to data obtained photographically in the region in which lie the absorption bands of the various halogenoplatinates.

In Fig. 4 the solid line represents the calculated absorption spectrum of a solution containing **39.2%** of sodium bromoplatinate and 61.8% of sodium chloroplatinate. The circles give the observed absorption spectrum of a solution of sodium bromoplatinate to which enough sodium chloride had been added to make the "apparent % transformation" 61.8%. Since the two curves are entirely different, the colorimetric data of such a mixture are not a measure of actual concentrations, and intermediate complex ions must be present. Similar curves have been obtained for solutions of different concentrations, and for mixtures of iodo and bromoplatinates; for them the original thesis[2] must be consulted as they have been omitted to save space.

In this connection Fig. 5 is of interest. In it the solid line represents the absorption spectrum calculated for a mixture of potassium chloroplatinate and potassium bromoplatinate in the proportion corresponding to the formula $K_2PtCl_4Br_2$. The circles represent the absorption spectrum of this "compound prepared according to the method of Pitkin.[19] It will be seen that the spectrum[24] is identical with that calculated for the mixture, and that Pigeon's conclusion that compounds can be prepared in this way is not borne out by the facts. In this we have corroborated the work of Herty.[21]

This research is one of a series of investigations carried out with the aid of a grant from the Bache Fund of the National Academy.

Summary

1. It has been shown that to cause the reaction $PtBr_6^{=} + 6Cl^{-} \longrightarrow PtCl_6^{=} + 6Br^{-}$ to go 99% to completion there must be approximately 660 times as much chloride as bromide ion constituent in the solution. For the reaction between iodoplatinate and bromoplatinate ions there must be 25,000 times as much bromide as iodide ion constituent. From these data we have estimated that roughly 16,000,000 times as much chloride as iodide ion constituent must be present completely to convert $PtI_6^{=}$ to $PtCl_6^{=}$, and have confirmed this order of magnitude experimentally.

2. A study of the absorption spectra of the various equilibrium mixtures indicates that in these reactions intermediate compounds are formed in solution.

3. We have also shown that the solid intermediate compounds which have at various times been reported in the literature are really mixtures. This confirms the conclusions of other workers in this field.

CHICAGO, ILL.

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[24] The absorption spectrum was measured as soon as possible after dissolving the solid to prevent possible transformation in solution to mixed halogenoplatinates.

[CONTRIBUTION FROM BELL TELEPHONE LABORATORIES]

THE ATOMIC WEIGHT OF POTASSIUM FROM PLANT ASH

BY H. H. LOWRY

RECEIVED SEPTEMBER 19, 1930 PUBLISHED NOVEMBER 5, 1930

It has been reported by F. H. Loring and J. G. F. Druce[1] that the potassium from the ash of potatoes fertilized from potassium chloride has an atomic weight of 40.5. The accepted atomic weight of potassium is 39.10.[2] It is known that normal potassium consists of two isotopes, 39 and 41, and the small beta radioactivity of potassium has been ascribed to the isotope of atomic weight 41. Loring and Druce cite Zwaardemaker's work[3] on the importance of radioactive material in maintaining life and were led to their experiment from a consideration of the well-known fact that plant cells selectively absorb potassium salts from solutions containing both potassium and sodium. If it is assumed that the reason for this selective absorption is the need of the plant for the radioactive isotope of potassium, it is reasonable to expect that some mechanism may have been developed by the plant cells to absorb selectively the radioactive isotope of potassium from the normal mixture of isotopes. It may be further assumed that the radioactive isotope would be concentrated in those cells which provide the food for the embryo plant, *i.* e., the seeds. To check these hypotheses 25 pounds of cotton—seed hairs—and 75 pounds XXXX Superfine flour—wheat kernels—were ashed, the potassium chloride separated from the ash and purified and the ratio of potassium to chlorine determined.

The ashing was carried out at a low temperature to avoid volatilization of the potassium salts. The ash was extracted with water and excess ammonium carbonate added. The extract was filtered, evaporated to dryness in platinum and the excess ammonium carbonate volatilized. The residue was dissolved in water, acidified with hydrochloric acid, filtered, re-evaporated to dryness, fused, redissolved in a small quantity of water and filtered. The alkali chlorides were then precipitated with hydrogen chloride gas, filtered and then fused. Preliminary analysis of the cotton ash showed a ratio of potassium to sodium of approximately 10 and this ratio for the wheat flour is approximately 40.[4] In the case of the chlorides from cotton ash approximately 20 g. of sodium-free potassium chloride was obtained by fractional crystallization of the aqueous solution at room temperature. It proved much more difficult to secure a pure potassium chloride from the flour ash and the procedure given above for the original purification, including the precipitation of the chlorides with

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[1] Loring and Druce, *Chem. News,* 140, **34** (1930).

[2] G. P. Baxter, THIS JOURNAL, 52, 861 (1930).

[3] Zwaardemaker, Arch. *Ges. Physiol., 213,* 82 (1926), and later papers.

[4] Bailey, "The Chemistry of Wheat Flour," 1925, p. 148.

hydrogen chloride gas and fusion, was repeated four times. Approximately 3 g. of sodium-free potassium chloride was finally obtained from the wheat flour ash. Analyses of the fused potassium chloride were made for chlorine using silver nitrate, making all precipitations and filtrations in the dark. Microscopic examination of a drop of solution allowed to crystallize on **a** slide showed no impurities. The percentages of chlorine obtained in multiple analyses of the two samples are given below.

Sample	Chlorine in KC1 from cotton ash, %
1	47.63
2	47.50
3	47.52
4	47.56
5	47.54
Av.	47.550 ± 0.016

Sample	Chlorine in KCl from wheat flour ash, %
1	47.57
2	47.52
3	47.60
Av.	47.563 ± 0.020

The ± figures given represent the probable errors calculated according to the method of Shewhart[6] for averages obtained from small samples.

Assuming the atomic weight of chlorine to be 35.457,[2] the atomic weights of the potassium may then be calculated to be 39.111 ± 0.013 from the cotton ash and 39.091 * 0.016 from the wheat flour ash, respectively. Both values are so close to the accepted value of 39.10 that no separation of the potassium into its isotopes is indicated.

The results reported above do not confirm the hypotheses proposed nor the results obtained by Loring and Druce. They cannot be used, however, as *a* direct contradiction of Loring and Druce's findings, since the potassium they obtained was from potatoes, which are morphologically different from the cotton fiber and the wheat flour.

I wish to acknowledge my appreciation of the careful analyses made by Messrs. H. W. Hermance and L. L. Kathan and the assistance of Mr. M. H. Quell in ashing the cotton and in the purification of the chlorides.

BELL TELEPHONE LABORATORIES
NEW YORK, N. Y.

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[5] **Shewhart,** *Bell System Tech.* **J.,5, 308 (1926).**

NOTES

A Condenser for Low Temperature Evaporation of Water.—In concentrating serums, gland extracts or any water solution containing protein, it is often advisable to evaporate the water at as low a temperature as possible. The ordinary vacuum distillation does not permit a distilling temperature below 35°. Even at 20° there may be denaturing, precipitation or destruction of biological activity due to combined exposure to temperature and mechanical agitation of boiling.

We have two condensers each containing, as inner tube, a glass tube $1^5/_8$ inch in diameter and 12 feet long (standard 2 inch iron pipe jacket), and these may be cooled by ice water; 12-liter pyrex flasks serve as retorts. While this is very effective, the distilling temperature can hardly be below 15°. The cooling water cannot be used below 0°, by adding salt to the ice, because an ice plug will block the condenser. Moreover, the heat absorption of the 40-gallon ice tank, the circulating pump, etc., make the system uneconomical for small quantities.

We find a 12-liter flask filled with crushed ice a very effective condenser. This eliminates necessity for transmitting heat through a glass or metal condenser surface; moreover, salt may be added to the ice, giving an effective condensing temperature below −10°. Theoretically, to condense 1 g. of water vapor at 0° requires melting 7.5 g. of ice, and in practice more is required. The 12-liter condenser may be insulated with rags or shavings, and there is little heat absorption from the atmosphere, because of its compactness. A specially long rubber stopper prevents danger of sucking in. The stopper has a large inlet for water vapor and a small inlet for vacuum; by making the tubes concentric, one reduces the tendency of the stopper to leak. We have used iron pipe for the tubes. A 2-liter flask with not more than 1 liter to be evaporated serves as "retort," but if the liquid foams badly a larger flask may be used. The connection to the "retort" should be 0.5 inch or preferably more inside diameter, and as short as possible.

The distilling rate is slow. Thus with outside water-bath at 20° and 700 cc. of water in the "retort," about 2 cc. per minute distils (temp. inside "retort," 7°). When first connected the distilling rate is faster and a layer of ice quickly freezes over the surface in the "retort," but this ice melts after the dissolved air is removed. If a slow stream of air bubbles into the "retort" through the usual capillary tube made by drawing out a broken thermometer, the retort temperature is lowered with an increase to about 3 cc. of water distilled per minute, and it is easier to keep ice in the "retort." In any case the distillation slows down near the end, due to decrease in heat transmitting surface, so that about ten hours may be required to reduce 700 cc. to 50 cc. (If a bath temperature of 25 or 30° is permissible the time is much reduced.)

A slow stream of tap water suffices for "heating" the bath of the "retort." We use a Nelson two-stage vacuum oil pump of a capacity of 5 cu. ft. of free air per minute for vacuum, for the high capacity saves many minutes in starting and eliminates the necessity for bothering about leaks around rubber stoppers. If the bath is heated by a flame, one must watch for a rise in temperature near the end of the evaporation, when the rate has slowed down.

For a capacity of, say, two 12-liter flasks in parallel as "retorts," each containing, say, 7 liters of serum, a condenser of a capacity of 25 to 30 gallons is required. Such steel tanks are used commercially for hot water storage, and may be insulated with 6 inches or more of shavings. If used only occasionally one may use a commercial insulated hot water storage tank, as the insulation dries out when not in use, but an insulation which does not easily rot should be selected. On this scale a vacuum pump of several cubic feet per minute capacity of free air should be used. Tubing for carrying the water vapor should be 1.25 inch or preferably more in diameter. The vacuum pump must naturally give better than the vapor pressure of water at $-10°$, under *service* conditions. Naturally one will select a condenser giving a large surface above the ice and salt, to increase the condensing rate. The operator should guard against possible serious injury due to collapse of a 12-liter flask under vacuum.

BERKELEY, CALIFORNIA

H. M. EVANS
R. E. CORNISH
J. C. ATKINSON

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PUBLISHED NOVEMBER 5, 1930

Inorganic Lubricants. III. Mixtures of Aqueous Liquids with Non-Reacting Solids.—When water is mixed with a finely divided insoluble powder in the correct proportions a cream is produced which has the power of forming a thin, continuous film over a surface capable of being wet by water, is "viscous" in proportion to the amount of solid present, and so may act as a lubricant between two moving surfaces.[1] For purely temporary inorganic lubrication such a mixture may operate satisfactorily, but because the water quickly evaporates, leaving a non-lubricating cake of solid, lasting lubrication is not obtained.

When, however, a hygroscopic inorganic liquid, such as a concentrated aqueous solution of a deliquescent salt or acid, is employed instead of water, drying out does not take place, the creamy state persists and lubrication is maintained for an indefinite length of time depending on the relation between the average atmospheric humidity and the relative hygroscopicity of

[1] See, for example, various U. S. Patents, such as Colby, 49,983, Sept. 19, 1865; Farkas, 1,253,362, January 15, 1918, and others.

the liquid. I have prepared many such mixtures, using solutions of calcium, zinc and ferric chlorides, antimony pentachloride,[2] sulfuric and orthophosphoric acids and similar substances as liquids, and kaolin, bentonite, talc, graphite, carbon, precipitated silica, etc. (all sieved to pass a 100-mesh screen), as the non-reacting insoluble solids. Bentonite and talc could not be used with acid liquids because a gas-forming reaction takes place resulting in a frothy mixture. Successful lubricants were obtained in considerable variety. Typical examples are listed in Table I.

TABLE I

LUBRICATING MIXTURES

10 g. of solid used in each experiment

Solid	Kaolin	Kaolin	Kaolin	Bentonite	Graphite	Silica
Soln., 50% concn. of	H_2SO_4	$CaCl_2$	$ZnCl_2$	$CaCl_2$	$CaCl_2$	$ZnCl_2$
Cc. taken	6.0	6–6.5	6.5	8 0	6.5	6.5

MATERIALS.—The kaolin was the N. F. V. product; the silica was an anhydrous, amorphous material (electro-silicon); the bentonite and graphite were fine, commercial powders; and the calcium and zinc chloride solutions were prepared from anhydrous *c.* P. granules.

Of all the mixtures prepared, the best for general use were those of kaolin and of graphite with calcium chloride solution. After three months, although exposed surfaces of these mixtures had fluctuated in liquidity considerably, lubricating films between ground glass surfaces still operated satisfactorily.

Lubricants of this general kind are distinctly limited in usefulness. Their pasty nature permits clogging of small passages; and too great pressure may thin the lubricating film excessively. Nevertheless, they are useful in organic work when protection against leakage of water-insoluble organic liquids and gases is desired; and some of them can be employed with certain inorganic gases (such as those which may attack the common organic lubricants), particularly when it is not important to maintain great purity of these gases. They offer the advantage of being easily and quickly prepared; and the range of possible mixtures is wide enough to permit a considerable degree of choice in both liquid and solid constituents and so enable any specific requirements to be more suitably met.

CONTRIBUTION FROM THE
CHEMICAL LABORATORIES OF HARVARD COLLEGE
CAMBRIDGE, MASSACHUSETTS

WILLIS A. BOUGHTON

RECEIVED JUNE 4, 1930
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[2] Mixture of antimony pentachloride solution and kaolin forms a colloidal material, the properties of which will be investigated.

The Constricted Mercury Arc.—The usefulness of the highly intense constricted mercury arc has been seriously limited by its rapid rate of deterioration.[1] The arc described here has been designed to balance the various factors so that it can be burned at a constant high intensity.

A quartz capillary 2 X 8 X 50 mm. was ground on the side away from the slit until a wall of about 0.5 mm. remained. The other side was ground until a face of about 3 mm. width was obtained, thus reducing the apparent size of the capillary. A very satisfactory polish was then obtained on both sides by cleaning with hydrofluoric acid and heating carefully with a sharp flame. A piece of glass tubing was ground open the length of the capillary and fitted to the rear flat side of the lamp in order to cool with running water. The lower electrode was sealed in with de Khotinsky cement. The lamp was wrapped with strips of cloth so that cooling of the cement and electrodes could be efficient and convenient. A stream of air was passed around the front face. By this arrangement the lamp could be run at 4–5.5 amperes and 20–25 volts per sq. cm. for upward of thirty hours with fairly constant intensity. At the expense of rapid devitrification (fifteen to twenty hours) the intensity can be kept constant by no air cooling on the front face, which prevents the formation of silica patches. A fairly constant intensity can be maintained by an intermittent air stream easily arranged by a long lag relay circuit. In case any deposit forms on the front side it can be removed quickly by stopping the air stream and moderately increasing the amperage.

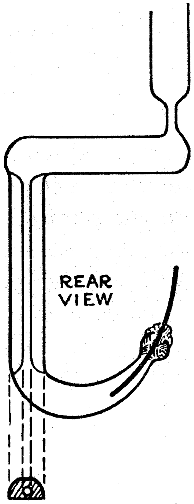

Fig. 1.—Lower electrode is sealed in with de Khotinsky cement. Constriction at upper electrode fits inserted iron wire or is packed with additional pieces to steady the upper meniscus.

Columbia University
New York City

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R. H. Crist

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[1] Forbes and Harrison, This Journal, 47, 2449 (1925); Langer and Meggers, *Bur. Stds. J. Res.*, [5] 4, 711 (1930).

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

THE DECOMPOSITION OF MERCAPTANS IN ALKALI SOLUTIONS[1]

BY E. C. BILLHEIMER[2] AND E. EMMET REID

RECEIVED MARCH 18, 1930 PUBLISHED NOVEMBER 5, 1930

Introduction

It is a well-established fact that the structure of the group attached to a carbon atom in combination with oxygen or a halogen has a great influence upon the strength of that bond. This has been shown by Conant and his associates,[3] who investigated the relation between the structure of organic halides and the speed of their reaction with inorganic iodides, and by Norris and his co-workers,[4] who studied the relative reactivities of the hydroxyl hydrogen atoms in certain alcohols and the effect of various substituted groups on the strength of the carbon–chloride bond.[5] It was thus considered of value to determine the effect of the structure of the alkyl group upon the strength and reactivity of the carbon–sulfur bond, and for this purpose the decomposition reaction of the aliphatic mercaptans in alkali solution was selected. It was desired to determine (1) whether mercaptans decompose in alkaline solution in any definite and reproducible manner, *(2)* the effect of time, temperature and concentration on this reaction, and **(3)** the exact course of the reaction, the products formed, and if possible its velocity constant and temperature coefficient.

Results

The aliphatic mercaptans were found to decompose in sodium hydroxide solution in a definite and reproducible manner. Three simultaneous reactions take place as follows: (1) replacement of the —SH group by hydroxyl to form an alcohol, as

$$RSH + 2NaOH = ROH + Na_2S + H_2O$$

(2) elimination of hydrogen sulfide from two molecules of mercaptan to form the alkyl sulfide, as

$$2RSH + 2NaOH = R_2S + Na_2S + 2H_2O$$

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[1] Presented at the Columbus Meeting of the American Chemical Society, May 1, 1929.

[2] From the Ph.D. dissertation of E. C. Billheimer, June, 1929.

[3] Conant and Kirner, THIS JOURNAL, 46, 232 (1924); Conant and Hussey, *ibid.*, 47, 476 (1925); Conant, Kirner and Hussey, *ibid.*, 47, 488 (1925).

[4] Norris and Ashdown, *ibid.*, **47**, 837 (1925); Norris and Cortese, *ibid.*, 49, 2640 (1927).

[5] Norris and Morton, *ibid.*, 50, 1795 (1928); Norris and Banta, *ibid.*, 50, 1804 (1928); Norris and Blake, *ibid.*, 50, 1808 (1928); Norris and Gregory, *ibid.*, 50, 1813 (1928).

(3) the elimination of hydrogen sulfide from one molecule of mercaptan to form the unsaturated hydrocarbon, as

$$CH_3CH_2SH + 2NaOH = CH_2{=}CH_2 + Na_2S + 2H_2O$$

Two further possible consecutive reactions, in which the alkyl sulfide might decompose with alkali to produce either the alcohol or the unsaturated hydrocarbon, were shown to be unimportant, as they are not given by butyl sulfide heated under the same conditions. The products of the three reactions were identified. The alkyl sulfide was oxidized to the corresponding sulfone with fuming nitric acid, according to the method of Grabowsky,[6] the product purified and identified by its melting point, which was compared with that of pure sulfone prepared in a similar manner from the particular sulfide in question. The alcohol was shown to be present by the formation of the corresponding half-ester of phthalic acid, on refluxing with phthalic anhydride, a dried benzene extraction of a steam distillate of the reaction mixture, from which the unreacted mercaptan had been removed by precipitation as mercaptide with lead acetate solution. The product was subsequently isolated and purified, and its identity proved by melting point determinations. The unsaturated hydrocarbon was easily noticeable in the case of the lower members of the mercaptan series, when it escaped as a gas, especially with ethyl mercaptan, in which case ethylene was evolved upon opening the bomb after a run. The sodium sulfide was easily distinguished by the evolution of hydrogen sulfide upon acidification.

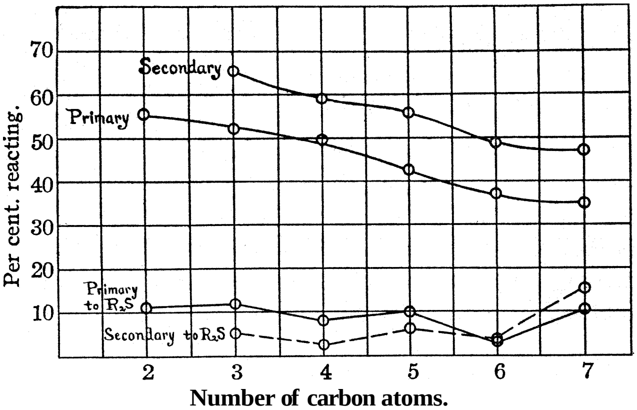

Fig. 1.—Percentage of mercaptans reacting with 3 N NaOH in 2 hours at 260°.

The optimum conditions for comparison of the reactivity of the different members of the mercaptan series were established with n-butyl mercaptan. They were *so* adjusted, by varying concentration, temperature and time of heating, that about half of this mercaptan was decomposed, which is the

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[6] Grabowsky, Ann., 175, 348 (1875).

case in two hours at 260° with 3*N* caustic soda solution. The runs for comparison of different mercaptans were made under these conditions. Runs with other concentrations of alkali and at other temperatures were made for other comparisons. The straight chain primary and secondary mercaptans from ethyl and isopropyl to heptyl have been studied. It was intended to include the octyl and nonyl mercaptans but their sodium derivatives were found to be insoluble, separating out immediately upon addition of the mercaptan to the alkali. This prevented complete solution of the products of the reaction at the completion of a run, and made it impossible to secure the aliquots necessary for the analytical procedure.

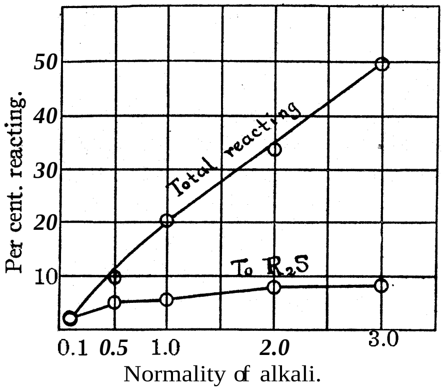

Fig. 2.—Percentage of n-butyl mercaptan reacting with different strengths of alkali.

The results are given in the tables below, the figures being the average percentages of the mercaptans reacting under the conditions stated. The same data are reproduced in the curves, Fig. 1 and Fig. 2.

It appears that the total decomposition decreases, with both normal and secondary mercaptans, as the number of carbon atoms increases. There is a suggestion of alternation. The secondary mercaptans react more rapidly

TABLE I

NORMAL MERCAPTANS WITH 3*N* SODIUM HYDROXIDE (2 HOURS AT 260°)

Mercaptan	Et	Pr	Bu	Iso-Bu	Am	Hex	Hep
Total decomposed	55.4	52.2	49.6	36.2	42.9	37.0	35.0
R_2S formed	11.0	12.1	8.1	6.1	9.9	3.1	10.4
Percentage R_2S	20	23	16	16	23	8	30

TABLE II

β-SECONDARY MERCAPTANS WITH 3N SODIUM HYDROXIDE (2 HOURS AT 260°)

No. carbon atoms	3	4	5	6	7
Total decomposed	65.4	59.1	56.0	48.8	47.0
R_2S formed	5.2	2.6	6.3	3.6	15.3
Percentage R_2S	8	4	11	7	33

TABLE III

VARIATION OF DECOMPOSITION OF *n*-BUTYL MERCAPTAN WITH CHANGES IN STRENGTH OF THE ALKALI

Concn. of NaOH	0	0.1	0.5	1.0	2.0	3.0
Percentage decomposed	0.0	2.1	9.8	20.2	33.8	49.6
R_2S formed	0.0	1.7	4.9	5.4	7.8	8.1
Percentage R_2S	...	81	50	27	23	16

TABLE IV

DECOMPOSITION OF *n*-BUTYL MERCAPTAN AT DIFFERENT TEMPERATURES BY 3 N SODIUM HYDROXIDE

Temperature, °C.	250	250	260	270
Time in hours	2	4	2	2
Percentage dec.	30	47.2	49.6	63.0
R_2S formed	7.7	31.9	8.1	8.2
Percentage R_2S	26	25	16	13

than the corresponding primary, which is to be expected from the work of Norris and his co-workers, who found that reactions of alcohols in which the hydroxyl is eliminated proceed faster with secondary alcohols than with primary. The amount of sulfide formed is lower with the secondary than with the primary, which agrees with the above. With very dilute alkali the percentage of alkyl sulfide is high when it is compared with the total decomposition. Isobutyl mercaptan reacts much more slowly than *n*-butyl, just as in esterification. At 250° in four hours n-butyl mercaptan gives slightly less decomposition than at 260° in two hours, which shows that the reaction has about the usual temperature coefficient. The proportion of butyl sulfide formed is somewhat higher at the lower temperature.

There is a suggestion of alternation, the values for the mercaptans having an even number of carbon atoms appearing to be below the curve,

Apparatus and Materials

The special apparatus necessary for and used in the preliminary part of this investigation was exactly similar to that employed by Herndon and Reid[7] in work on the decomposition of organic compounds at high pressures and temperatures, which was itself a modification of the type developed by Morey[8] in his studies on hydrated silicates. This consisted of the special steel bomb, the furnace and the automatic temperature control. For the greater part of the present work, however, a smaller type bomb was used, of *25-cc.* capacity, with threads on the outside of the body proper, allowing easier and more complete removal of the reaction products. The plunger rested atop the body proper and carried through its center a steel thermocouple tube silver-soldered to the plunger and extending a half inch into the chamber of the bomb when the latter was closed.

The mercaptans, with the exception of ethyl, n-butyl and isobutyl, were furnished by L. M. Ellis, Jr.9 Normal butyl mercaptan, which was used to standardize the analytical method and establish the proper conditions for comparison, was prepared in large quantities by the method of Grabowsky and Saytzeff.[10] The mercaptan was extracted with dilute caustic soda solution, recovered by steam distillation, dried and fractionated on a tall-column still. The purity was 99.94%. The ethyl and isobutyl mercaptans were Eastman's "Certified" products. The purity of the normal and secondary mercaptans used was in no case less than 99.3%.

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[7] Herndon and Reid, THIS JOURNAL, 50, 3066 (1928).

[8] Morey, *ibid.*, 36, 215 (1914).

[9] Ellis, "Dissertation," Johns Hopkins University, 1929.

[10] Grabowsky and Saytzeff, Ann.. 171, 251 (1874).

Experimental

The purity of the mercaptans was determined volumetrically by the method of Kimball, Kramer and Reid[11] which makes use of their reaction by titration with standard iodine solution. This reaction was also made the basis of the analytical method eventually established. The procedure was essentially as follows. The reaction mixture was washed from the bomb into a separatory funnel, from which the water layer was run into a volumetric flask and diluted to a convenient volume. The insoluble alkyl sulfide was measured and its weight calculated from its density. From the water solution aliquots were taken. First, one aliquot was titrated with 6 N hydrochloric acid, using methyl orange as an indicator, to determine the amount of acid necessary to neutralize the excess alkali and decompose the sodium sulfide formed. Second, an aliquot was run from a pipet with its tip below the surface of excess standard iodine solution containing hydrochloric acid in slight excess of that determined by the first operation and the excess iodine titrated with standard thiosulfate solution. This gave a value for the sum of the sodium sulfide and the unreacted mercaptan. Third, an aliquot was boiled to remove all unreacted mercaptan, diluted with water and boiled several times if necessary, and the hydrogen sulfide formed in the decomposition thus determined by washing into excess iodine solution containing the predetermined amount of hydrochloric acid and back-titrating with thiosulfate solution as before. These three sulfur values, namely, the alkyl sulfide, sodium sulfide and unreacted mercaptan, when calculated to mercaptan, gave a check on the amount originally added, and from them could be determined the percentage decomposition, since all three reactions produce sodium sulfide.

TABLE V

EXPERIMENTAL RESULTS

Col. 1, mercaptan reacted, %; Col. 2, sodium sulfide formed, %; Col. 3, mercaptan unreacted, %; Col. 4, alkyl sulfide formed, %; Col. 5, mercaptan accounted for, %.

	(1) Ethyl mercaptan, 2 hrs., 260°						(2) n-Propyl mercaptan, 2 hrs., 260°				
	55.5	48.7	39.1	10.9	98.7		52.3	43.3	39.4	12.5	95.2
	55.0	46.5	38.2	10.8	95.5		52.6	42.8	38.6	12.7	94.2
	55.7	48.0	38.2	11.2	97.3		51.8	44.1	41.0	11.0	96.1
Av.	55.4	47.7	38.5	11.0	97.2	Av.	52.2	43.4	39.7	12.1	95.2

	(3) n-Butyl mercaptan, 2 hrs., 260"						(4) Isobutyl mercaptan, 2 hrs., 260°				
	50.0	45.0	45.0	8.1	98.0		35.9	33.4	59.5	6.4	99.2
	49.4	44.6	45.7	8.1	98.5		36.5	33.9	59.0	5.8	98.8
	50.1	44.6	44.2	8.7	97.4		35.8	33.5	59.9	5.2	98.7
	48.8	43.2	45.4	7.5	96.2		36.1	33.0	58.4	6.4	97.9
	49.7	44.7	45.4	8.1	98.3		36.6	33.7	58.4	6.9	98.9
Av.	49.6	44.4	45.1	8.1	97.7	Av.	36.2	33.5	59.0	6.1	98.7

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[11] Kimball, Kramer and Reid, THIS JOURNAL, 43, 1199 (1921).

TABLE V (Continued)

(5) *n*-**Amyl** mercaptan, 2 hrs., 260°

	42.5	37.0	50.1	10.7	97.7
	42.9	38.1	50.6	10.1	98.9
	43.3	39.6	51.7	8.4	99.5
	42.8	37.5	50.0	10.7	98.1
	43.2	37.7	49.7	9.5	96.8
Av.	42.9	38.0	50.4	9.9	98.2

(6) *n*-**Hexyl** mercaptan, 2 hrs., 260°

	37.1	35.4	60.2	3.2	98.8
	37.3	35.8	60.3	3.5	99.6
	36.5	35.0	60.6	2.7	98.3
Av.	37.0	35.4	60.4	3.1	98.9

(7) n-Heptyl mercaptan, 2 hrs., 260°

	35.0	30.4	56.4	10.6	97.3
	35.2	31.1	57.3	10.1	98.5
	34.8	30.5	57.1	10.4	98.1
Av.	35.0	30.7	56.9	10.4	98.0

(8) Isopropyl mercaptan, 2 hrs., 260'

	65.7	61.0	32.0	5.6	98.5
	65.0	61.2	32.9	5.0	99.1
	65.4	61.4	32.5	5.0	98.8
Av.	65.4	61.2	32.5	5.2	98.8

(9) *Sec.*-**butyl** mercaptan, 2 hrs., 260'

	58.8	56.2	39.4	3.0	98.6
	59.2	56.8	39.3	3.0	99.1
	59.3	57.2	39.0	2.5	98.7
	59.0	56.9	39.6	1.9	98.4
	59.3	56.8	38.9	2.5	98.3
Av.	59.1	56.8	39.2	2.6	98.6

(10) *Sec.*-**amyl** mercaptan, 2 hrs., 260°

	56.5	51.6	39.7	7.2	98.4
	56.0	52.2	40.8	6.2	99.2
	55.6	52.6	41.9	5.1	99.5
	56.3	51.8	40.4	6.2	98.5
	55.8	53.3	42.2	6.8	99.9
Av.	56.0	52.3	41.0	6.3	99.1

(11) *Sec.*-**hexyl** mercaptan, 2 hrs., 260"

	48.9	46.1	48.3	3.8	98.1
	48.3	45.6	48.8	3.5	97.9
	49.1	46.5	48.7	3.5	98.7
Av.	48.8	46.1	48.6	3.6	98.2

(12) *Sec.*-**heptyl** mercaptan, 2 hrs., 260°

	46.7	38.1	43.5	14.4	96.1
	47.0	38.3	43.2	15.2	96.7
	47.3	38.3	42.8	16.2	97.3
Av.	47.0	38.2	43.2	15.3	96.7

(A) n-Butyl mercaptan, 2 hrs., 250°

	30.1	26.8	62.2	7.5	96.4
	30.2	26.6	61.5	8.0	96.1
	29.5	25.6	61.5	7.5	94.8
	29.1	25.5	62.2	7.5	95.3
	30.9	27.3	61.0	8.0	96.4
Av.	30.0	26.4	61.7	7.7	95.8

(B) n-Butyl mercaptan, 4 hrs., 250°

	46.8	40.0	45.4	12.8	98.1
	46.3	38.7	45.0	11.6	95.3
	47.5	41.3	45.6	11.6	98.5
	48.8	42.2	44.3	12.2	98.7
	46.6	40.5	46.6	11.1	98.2
Av.	47.2	40.5	45.4	11.9	97.8

(C) n-Butyl mercaptan, 2 hrs., 270°

	63.0	56.5	33.2	8.7	98.3
	63.2	57.1	33.4	8.1	98.6
	62.9	57.3	33.9	8.1	99.2
	63.3	56.9	32.9	8.7	98.4
	62.8	57.5	34.1	7.5	99.1
Av.	63.0	57.1	33.5	8.2	98.7

TABLE V (Concluded)

The following runs were made between n-butyl mercaptan and sodium hydroxide solution of the following strengths: 2.0, 1.0, 0.5, 0.1 *N*, and finally pure water. The heating was for two hours at 260°.

n-Butyl mercaptan, 2.0 N NaOH

	33.8	30.3	59.3	7.7	97.4
	34.1	30.5	59.0	8.7	98.2
	33.4	30.0	59.9	7.1	97.1
Av.	33.8	30.3	59.4	7.8	97.6

n-Butyl mercaptan 1.0 N NaOH

	20.5	18.6	72.0	5.2	95.8
	19.8	17.9	72.4	5.1	95.4
	20.4	18.5	72.3	5.9	96.7
Av.	20.2	18.3	72.2	5.4	96.0

n-Butyl mercaptan 0.5 *N* NaOH

	9.9	9.0	81.9	4.6	95.4
	10.0	9.2	81.6	5.2	95.9
	9.4	8.7	82.2	4.9	95.7
Av.	9.8	9.0	81.9	4.9	95.7

n-Butyl mercaptan 0.1 N NaOH

	2.5	2.3	92.2	1.8	96.3
	1.9	1.8	95.2	1.6	98.7
	2.0	1.9	93.9	1.8	97.7
Av.	2.1	2.0	93.8	1.7	97.6

The amount of mercaptan used in each run was always 10 millimoles, which was dissolved in 12 cc. of the sodium hydroxide solution, which for the *3N* was 3.66 equivalents. This was a convenient sized charge since the bomb held 25 cc. The results obtained are given in Table V.

In the runs with pure water, the percentage of mercaptan reacted was found to be practically zero.

Summary

1. Apparatus has been developed and a quantitative method of analysis established for the investigation of the decomposition of mercaptans in alkali solution.
2. Mercaptans have been found to decompose in alkali solution in a definite and reproducible manner.
3. The course of the decomposition has been determined and the products identified.
4. This decomposition reaction has been used as a means of studying the effect of substitution on the reactivity of the C—S bond, and the following mercaptans have been investigated in this way: ethyl, n-propyl, isopropyl, n-butyl, isobutyl, *sec.*-butyl, n-amyl, *sec.*-amyl, n-hexyl, *sec.*-hexyl, n-heptyl, *sec.*-heptyl, n-octyl, *sec.*-octyl, *n*-nonyl, *sec.*-nonyl.
5. The effect of concentration of alkali on the rate of decomposition of the mercaptans has also been determined.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE PURE OIL COMPANY]

AUTOXIDATION OF THE AMYLENES[1]

BY JULIUS HYMAN AND C. R. WAGNER

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A. Introduction

Although considerable work has already been done on the various phases of autoxidation, the field is of such magnitude that the special divisions of the subject suffer through lack of sufficient definite information concerning details.

One such division has to do with the autoxidation of the cracked gasolines. Much work still remains undone in this field. The chief reason for our lack of scientific knowledge in this especial field lies in the complex nature of the experimental material, namely, cracked gasoline. Such gasoline is doubtless a combination of paraffin, olefin, cyclic and aromatic hydrocarbons, along with hydrocarbons possessing in single molecules the characteristics of two or more of the classes mentioned.

In view of the situation as just presented, the authors of this paper felt that a study of the autoxidation of a comparatively simple series of olefins—the hydrocarbons with which autoxidation in gasolines appears most closely allied—might shed further light on the nature of the autoxidation phenomenon. Chief among the questions which such a study might answer is the one concerning the relation of autoxidation reactivity to the position of the double bond in the molecule, *i. e.*, to the nature and position of the groups attached to the unsaturated carbon atoms.

The simplest of such groups would be the butylenes, which number three. These compounds, however, are gaseous at ordinary temperatures, and in view of the fact that autoxidation in cracked gasolines appears to occur mainly in the liquid phase, it was thought unwise to use these materials in the present work.

The first group of olefins which are liquid at ordinary temperatures is that of the amylenes, five in number. These five are: (1) *n*-propylethylene, (2) isopropylethylene, (3) unsymmetrical methylethylethylene, (4) symmetrical methylethylethylene, (5) trimethylethylene.

The first systematic work on this group appears to have been done by Norris and Joubert.[2] These authors investigated the polymerizing action of sulfuric acid at various concentrations on the individual amylenes and found distinct differences in reactivity. Numbers 5 and 3 were classed as most reactive, Numbers 1 and 4 taking an intermediate position, while Number 2 was found to be comparatively unreactive.

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[1] Presented before the Petroleum Division of the American Chemical Society at Atlanta, Georgia, April 7–11, 1930.

[2] Norris and Joubert, THIS JOURNAL, 49, 873 (1927).

Work by Kirrmann,[3] however, cast doubt upon the reality of amylene No. 1 used by Norris and Joubert. In the present work, therefore, the authors have prepared amylene No. 1 by the interaction of allyl bromide on the Grignard reagent, ethylmagnesium bromide, using butyl ether as well as the amyl ethers as solvents and diluents. The reaction produced an amylene of boiling point 29–31°, in accord with the results of Kirrmann, as opposed to those of Norris and Joubert, who claimed a boiling point of 39–41°, for the product. It is likely that in the purification of their material, the last-named authors caused their amylene to undergo an intramolecular rearrangement of some type.

B. Experimental

In the present work amylenes 4 and 5 were made according to the methods given by Norris and Joubert. In the preparation of (5) heed was taken of the warning of Norris and Reuter[4] that in the dehydration of *tert.*-amyl alcohol a certain amount of amylene 3 is formed, and only the fraction boiling between 37.5 and 39° was used. Its D-line refractive index at 15° was 1.3898. The preparation of (4) appears to take place without any very great amount of side reaction. The fraction boiling between 35.5 and 37.5° was used in our experiments. The D-line refractive index at 15° for amylene No. 4 was 1.3840.

Amylenes 2 and 3 were made by the action of alcoholic potash on 1-iodo-3-methylbutane[5] and 1-iodo-2-methylbutane,[6] respectively, which had previously been prepared from their respective alcohols. Number 2 showed a boiling range of 21 to 24°, whereas No. 3 boiled almost constantly at 31.1°. Amylene No. 2 was further purified for Run No. 2 (see table) by treatment with 2:1 sulfuric acid at 0°. In this way a product of boiling range 20.5–21.5° was obtained. The D-line refractive index at 15° was 1.3682. The D-line refractive index for amylene No. 3 at 15° was 1.3800.

Amylene No. 1 was prepared as previously described. It was kept in contact with silver acetate in water over a period of weeks, with repeated distillations. Despite this, however, the product still showed a trace of bromine compound. Amylene No. 1 was finally freed from bromides by refluxing for four hours with metallic calcium and redistilling. It showed an almost constant boiling point of 30.0° (corr.). A refractive index determination at 21° gave a value of 1.3718 as compared with Kirrmann's value of 1.3714 for the same temperature. The refractive index reading (D-line) at 20° was 1.3731. An interesting side reaction in the production of amylene No. 1 was the formation of a hydrocarbon possessing a boiling point of around 20°. A fraction boiling between 20 and 24° was isolated.

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[3] Kirrmann, *Bull. soc. chim.*, 39, 988 (1926).

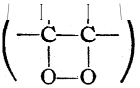
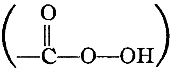
[4] Norris and Reuter, THIS JOURNAL, 49, 2624 (1927).

[5] Wischnegradsky, *Ann.*, 190, 361 (1878).

[6] Le Bel, *Bull. soc. chim.*, [2] 25, 546 (1876).

This fraction decolorized alkaline potassium permanganate very rapidly, and combined with bromine in the cold extremely energetically. While the exact nature of this compound is not known, it would appear probable that one is dealing in this instance with a substituted cyclopropane, probably ethylcyclopropane.

As to the method of determining the degree of oxidation, it was at first held expedient to use a manometric method, the lowering of the pressure in the reaction chambers being an indication of the amount of oxidation. During the course of the work, however, such erratic results were obtained that this method had to be abandoned. In its place was substituted a method based on the liberation of iodine by the bound (peroxide) oxygen.

According to the per-acid theory of autoxidation as suggested by us,[7] such oxidation proceeds in two steps: (1) the formation of a "moloxide"  $\left(\begin{array}{c} -\overset{|}{C}-\overset{|}{C}- \\ |\qquad| \\ O-O \end{array}\right)$ from the breaking down of an oxidized per-ester; (2) the formation of a per-acid  $\left(-\overset{O}{\overset{\|}{C}}-O-OH\right)$ through the oxidation of aldehydes produced by the breaking of a moloxide molecule.

Such per-acids are known to react with double bonds quite energetically, and the per-acid theory postulates a per-ester as the initial reaction product. Unless this cycle is completed, the theory does not allow for progressive autoxidation.

There is considerable evidence to show that peroxides of the type R—O—O—R—to which class moloxides are structurally related—are incapable of liberating iodine from hydriodic acid and, in accordance with this view, not the moloxides but only the per-acids and per-esters would oxidize the hydriodic acid. For comparative purposes in this study, therefore, the authors feel that this method for evaluating the relative extent of autoxidation is permissible.

One cubic centimeter of the amylene to be tested was pipetted from a cold pipet into an iodine flask to which had been added 20 cc. of a 5% alcoholic potassium iodide solution. To this mixture was added 2 cc. of glacial acetic acid, and the flask allowed to stand in the dark for exactly three minutes. The contents of the flask were then rapidly titrated against a 0.01 *N* sodium thiosulfate solution. As is well known, the starch indicator in an alcoholic solution takes on an orange tinge rather than the usual violet. The end-point of the titration is nervertheless very sharp. The iodine color usually reappears shortly after the titration has been completed. This is to be disregarded, however, if one wishes (as in the present case) merely comparative results.

As reaction chambers were used common four-ounce oil bottles, each containing ten pieces of 6-mm. glass tubing, 15 cm. in length (to promote surface oxidation) and being fitted with a good cork stopper. Ten cc. of sample was placed in each bottle, the

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[7] Wagner and Nyman, Annual A. P. I. Meeting, December, 1929; *J. Inst.* Pet. *Tech.*, 15, 676 (1929). Milas [*Proc. Nat. Acad. Sci.*, 14, 844 (1928)] had previously shown perbenzoic acid to act as an autoxidation catalyst for olefinic substances.

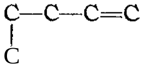
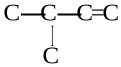
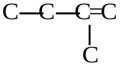
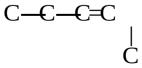
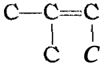
oxygen being introduced by a glass tube reaching half-way to the bottom of the bottles. The oxygen was taken from a tank and allowed to run in to each bottle for ten seconds. Thereupon the bottle was corked immediately and the contents thoroughly agitated. Whenever the bottles were opened, they were placed in an ice-bath, in order to maintain approximately constant conditions and to prevent evaporation as much as possible.

As oxidation catalyst cobalt oleate was used. This compound was prepared by dissolving 1 part of C. P. hydrated cobaltous acetate in 10 parts of hot U. S. P. oleic acid, and passing a current of air through the mixture for two hours at a temperature between **125** and 150°. The resulting product is a deep brown liquid which turns deep red upon standing. It is completely soluble in the amylenes. To each 10 cc. of amylene was added two drops (0.0424 g.) of the catalyst. The oxidation was carried out in the dark, at a temperature of 15°.

TABLE I

RESULTS OF EXPERIMENTS

Run No. 1

	Compound	Type	Cc. of 0.01 N $Na_2S_2O_3$ used after 11 hrs.	17 hrs.	35 hrs.	42 hrs.
1	n-Propylethylene	 $\underset{\underset{\displaystyle C}{|}}{C}{-}C{-}C{=}C$	0.10	0.15	0.15	0.15
2	Isopropylethylene	 $C{-}\underset{\underset{\displaystyle C}{|}}{C}{-}C{=}C$	.45	1.55	5.90	6.10
3	*Unsym.*-methylethylethylene	 $C{-}C{-}\underset{\underset{\displaystyle C}{|}}{C}{=}C$	.10	0.10	0.10	0.10
4	*Sym.*-methylethylethylene	 $C{-}C{-}C{=}\underset{\underset{\displaystyle C}{|}}{C}$	1.20	2.70	3.45	4.35
5	Trimethylethylene	 $C{-}\underset{\underset{\displaystyle C}{|}}{C}{=}\underset{\underset{\displaystyle C}{|}}{C}$	2.65	5.30	5.20	9.85
6	Blank of No. 5	......	0.00	0.00	0.00	0.00

Run No. 2

	13 hrs.	19 hrs.	36 hrs.	84 hrs.	156 hrs.	252 hrs.
1	0.00	0.00	0.00	0.00	0.00	...
2	.00	.00	2.90	11.60	22.15	...
3	.00	.00	0.00	0.00	0.00	0.00
4	1.65	2.85	3.75	7.70	18.00	15.10
5	1.65	3.00	4.80	8.80	19.75	16.90
6	0.00	0.00	0.00	0.00	0.00	0.00

C. Conclusion

Of the two runs, the second is to be considered as more accurately expressing the reactivities of the amylenes toward autoxidation. The long induction period for amylene No. 2 may be explained by its vigorous purification just prior to use. On the other hand, the lack of an induction period in the autoxidation of amylenes Nos. 4 and 5 may be ascribed to minute quantities of peroxide which may have formed in these olefins during a short period of standing before use. An interesting point to note is the high reactivity of the amylene No. 2, once oxidation had begun, and the lesser but similar orders of reactivity of amylenes Nos. 4 and 5. The disappearance of peroxide at 252 hours is also of considerable interest.

Most noteworthy, however, is the fact that the results here recorded appear to bear little or no relationship to the results of the sulfuric acid polymerization experiments of Norris and Joubert.

A theory has been developed to explain the results herein recorded, and will be published at a later date. From the present data, however, it may be concluded that the *average* internal double bond is much more prone to autoxidation than is the *average* end double bond. It would, therefore, follow that in diolefins the internal double bond would be the first to be attacked. As a matter of record, the authors have previously reported[7] acrolein as being an important constituent among the products resulting from the autoxidation of cracked gasoline, an observation which is in accord with experiments reported herein.

The present paper is intended by the authors as a report of general work on autoxidation now in progress. It is hoped that further details will be ready for publication in the near future.

D. Summary

1. The autoxidation of the amylenes has been investigated.

2. Results indicate that, in general, internal double bonds are more readily oxidized by molecular oxygen than end double bonds.

3. Kirrmann's method of preparation of pentene-1 has been confirmed. A new hydrocarbon obtained as a by-product of this reaction is mentioned.

35 EAST WACKER DRIVE
CHICAGO, ILLINOIS

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

THE USE OF NICKEL AS A CATALYST FOR HYDROGENATION

BY HOMER ADKINS AND HOWARD I. CRAMER

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The hundreds of papers and patents published on the use of nickel as a catalyst for the hydrogenation of organic compounds might well be considered to render unnecessary any extended research in this field. In spite of this profusion of publications and in a sense because of it, a beginning has been made in what is intended to be a systematic investigation of the use of nickel as a catalyst for the hydrogenation and condensation of organic compounds especially with regard to selective reaction, *i. e.*, the modification of the proportion of simultaneous reactions through control of the temperature, pressure, reaction medium and character of the catalyst. For a number of reasons it does not seem that here or now is a suitable place or time for a comprehensive review of the extensive literature on the use of nickel as a catalyst. It must suffice for the present to refer to some of the more prominent investigators such as Sabatier, Senderens, Mailhe, Ipatiev, Schrotter, Brochet, von Braun, Zelinsky, Armstrong and Hilditch, and to the American and German translations of Sabatier's "La Catalyse en Chimie Organique."[1] The German edition contains a valuable review of the literature, prepared by Dr. Hans Hauber for the period 1920 to 1926.

The use of pressures in the range of 50 to 300 atmospheres is usually referred to as the method of Ipatiev and is the one used in the present investigation.[2] It should be pointed out however that Ipatiev, in general, used temperatures of from 200–400°. These high temperatures with their accompaniment of serious side reactions, were necessary, we believe, because he used rather inactive catalysts. Ipatiev believed that the oxide rather than the metal was the real catalyst for hydrogenations. While this is questioned by Sabatier and many others, there can be no doubt that nickel oxide at the temperatures used by Ipatiev is active in promoting reactions other than hydrogenation.

In this paper are described the preparation of a satisfactory catalyst and experimental conditions under which some forty-five representative organic compounds have been hydrogenated to give good yields of various compounds.

The Apparatus.—The material to be reduced was placed in copper or glass bottles or "liners" having an internal volume of from 100 to 600 ml. Each liner bore a pin-hole in the side half-way between its top and bottom. The effective capacity, *i. e.*, the volume below the pin-hole was thus 50 to 300 ml. The glass liners were closed by a ground-glass joint and the copper ones by a cap screwing down against a lead gasket. The caps of both types of bottle were designed with a tube extending downward to accommodate the thermocouple well projecting from the head of the bomb. The bombs were made of chrome vanadium steel by the American Instrument Company of Washington, D. C., using the type of bomb closure described by Ernst.[3] One of the bombs had outside dimensions of 26.7 cm. long by 14 cm. diameter, and the other 42 cm. by 11.4 cm. The inside diameter was 6 cm. for both bombs, one having a depth of 16.5 cm. and the other of 31.5 cm. Each bomb bore in the head a thermocouple so well designed that the end of a thermocouple could be extended beyond the center of the reaction chamber. The thermocouples were of No. 20 iron—onstantan wire encased in 2-holed insulation tubes 4 mm. in outside diameter.

Lead gaskets were used in most instances for the bomb closure. Copper gaskets made of copper wire 3 mm. in diameter were used for pressures above 200 atmospheres. The bomb was placed in a horizontal position in a shaker similar in principle to the one described by Peters and Stanger.[4] The bombs were electrically heated using 110-volt *a.* c. current and nichrome wire 0.1 mm. in diameter. Two heating units for each bomb

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[1] "Catalysis in Organic Chemistry," by Sabatier and Reid, D. Van Nostrand Company, New York, 1922; "Die Katalyse in der Organischen Chemie," by Sabatier and Finkelstein, Akademische Verlagsgesellschaftm. b. H., Leipzig, 1927.

[2] Ipatiev, *Ber.*, 37, 2961 (1904); *J. Russ. Phys.-Chem. Soc.*, 36, 786 (1904); 42, 1557 (1910); Sabatier–Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Company, New York City, 1922, p. 206.

[3] Ernst, *Ind. Eng. Chem.*, 18, 664 (1926).

[4] Peters and Stanger, *ibid.*, 20, 74 (1928).

were used, each having a resistance of about 27 ohms. The temperature was controlled by a Leeds and Northrup potentiometer controller and recorder.

The valves and connections used were similar in design to those described by Ernst and were supplied by the American Instrument Company. The tubing was $^1/_4$-inch O. D. by $^1/_{16}$-inch I. D. of molybdenum steel. The gages were of the ordinary commercial type having ranges from 0 to 5000 or 0 to 10,000 pounds per square inch and were purchased from the United States Gauge Company, New York.

The Catalyst.—The procedure finally adopted for the preparation of a nickel catalyst was a development from that recommended by Reid and Rather.[5] According to their procedure 100 g. of infusorial earth was treated with a solution of 50 g. of nickel nitrate $[Ni(NO_3)_2 \cdot 6H_2O]$ in about 150 ml. of water, and the resulting moist mass added to a strong water solution of 60 g. of sodium carbonate, $Na_2CO_3 \cdot 10H_2O$, to precipitate the nickel as carbonate. The product was well washed, dried, reduced with hydrogen just below red heat and cooled in carbon dioxide. This method was modified in the following particulars: (1) the infusorial earth was digested with nitric acid before use because otherwise inactive catalysts were obtained; (2) the ratio of nickel to infusorial earth was doubled; (3) the precipitation of nickel carbonate was made at 70–80° in order to avoid loss of nickel salts during washing; (4) the reduction was carried out at 450° for one hour; (5) the catalyst was cooled and transferred in an atmosphere of hydrogen.

The procedure for the preparation of the catalyst was as follows: one-half kilo of infusorial earth, obtained from the Meyer Drug Company, St. Louis, was digested on the steam-bath for sixteen hours with enough nitric acid (d 1.4) to give a suspension of porridge-like consistency. This material, after dilution with an equal volume of water, was filtered on a Buchner funnel and washed repeatedly with distilled water until the wash water gave only a faint acid test. After being thoroughly dried at 110–120° it was pulverized and stored in glass-stoppered bottles.

One hundred grams of acid-washed infusorial earth was treated with a filtered solution of 100 g. of nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$, in 150–175 ml. of water, and the whole thoroughly mixed. The resulting paste, warmed to 70–80°, was poured into a filtered solution of 120 g. of sodium carbonate $(Na_2CO_3 \cdot 10H_2O)$ in 100 ml. of water, which had also been warmed to 70–80°. After thorough mixing with a large stirring rod, the material was filtered on a Büchner funnel and washed, first with 300 ml. of water in 75-ml. portions, taken from the filter, dispersed in 300–400 ml. of water and again sucked dry on a filter and washed with 300 ml. of water. The mixture was dried at 110–120° and stored in *dry* glass-stoppered bottles. The yield from such a preparation was 134 g. Considering that no nickel was lost in the preparation, this material contained by calculation 16% nickel. The product was reduced in a stream of dry hydrogen at 450°. The hydrogen was ordinary electrolytic hydrogen with no purification other than drying by passing through a calcium chloride tube. The reduction was carried out in a pyrex tube, 15 mm. by 40 cm. in length, heated in a small electric tube furnace. The hydrogen was passed through the catalyst at the rate of 10 to 15 ml. per minute. The temperature of the furnace was maintained at 450 ± 3°.

The tube containing the catalyst was removed from the furnace after reduction had proceeded for one hour, and allowed to cool to room temperature under a pressure of 1.004 atmospheres of hydrogen. The catalyst was then poured from the tube (through which a stream of hydrogen was rapidly passing) into the liner containing the material to be reduced. The air in the liner had been previously displaced with carbon dioxide. The liner was then closed, placed in the bomb, the latter closed and placed in the shaker, the system evacuated to 15 or 20 mm. and hydrogen introduced to the desired pressure. The shaker was then started at a rate of about 40 cycles per minute. There was a drop

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[5] Reid and Rather, This Journal, 37, 2116 (1915).

in pressure during the first few minutes but if the connections were all tight the pressure remained constant after ten minutes of shaking. The bomb was then heated to the desired temperature. About an hour was required for reaching 100° and about two hours for 200°. After the reduction was complete the bomb was allowed to cool to room temperature (eight to twelve hours), the liner removed and the catalyst filtered off under suction on a Jena sintered glass filter.

Standardization of the Apparatus.—The course of the reductions was followed by means of the drop in pressure of hydrogen in the system. The volume of hydrogen equivalent to a given drop in pressure on the gage was a function of the volume of the reaction mixture, of the liner and of the temperature of the gas in the bomb. In order to ascertain the amount of hydrogen equivalent to a given drop in pressure on the gage it was necessary to determine the drop in pressure which occurred when a known quantity of material was reduced. Such compounds as acetone, toluene and dimethylacetoacetic ester reduce quantitatively with no side reactions, so that they were used for the purpose of standardization. By means of various fillers, liners and volumes of reactants the drop in pressure per mole of hydrogen absorbed could be varied from 625 to 3000 pounds per square inch measured at 20°. The gages could be read with an accuracy of ten pounds or less. The loss of hydrogen due to diffusion and leaks was less than thirty pounds in the great majority of the experiments. That is to say, if the original pressure was 2000 pounds at 20° and the bomb was then heated to 200°, kept there for perhaps six hours and cooled to 20°, the pressure would be at least 1970 pounds, and in many cases would be 1990 or higher. It is safe to say then that in a successful experiment the drop in pressure of hydrogen was accurate to within considerably less than fifty pounds.

The temperature to be used for the reduction of a compound was usually decided upon as a result of observation of the increase in pressure in the svstem as the temperature of the bomb increased. If no reduction had occurred at a given temperature, the pressure would be within twenty or thirty pounds of that predicted by the gas laws. The beginning of reduction would be evidenced by an increasing divergence between the actual pressure and the calculated pressure for that temperature. There is no doubt that the pressures used are in numerous cases considerably above those necessary for satisfactory results. The relationship of pressure to the rate of reduction varies materially with different types of compounds and this matter will be considered in subsequent papers.

Solvents.—Solvents have been used by workers in this Laboratory to a greater extent than has been done by others using nickel catalysts. It therefore seems worth while to point out the merits of a few of the common solvents. Ether may be used up to 197° if the pressure is above forty atmospheres and methanol to 240° if the pressure is above eighty atmospheres. The other common solvents may be used to even higher temperatures with similar pressures, so that in so far as the boiling point of the solvent is concerned, there is no limitation on the practical use of any of the common solvents up to approximately 200°. The use of a solvent greatly facilitates the handling of the reaction mixture both during the introduction of the catalyst and in filtering it off after the reduction is complete.

The amount of hydrogen absorbed may be readily and accurately calculated from the drop in pressure in the system if the volume of reaction mixture is constant in a series of experiments. This may be most satisfactorily done by using a solvent for making the various mixtures up to constant volume. A solvent is sometimes advantageous for maintaining the homogeneity of the reaction mixture. For example, the reduction of diphenyl carbinol practically stopped with the formation of diphenylmethane because the water formed in the reduction of the alcohol formed an immiscible layer holding the catalyst out of contact with the diphenyl methane. In the presence of alcohol the reduction proceeded smoothly to dicyclohexylmethane. Conversely, it may be desirable to use as a solvent a compound which will give a non-homogeneous mixture with the reaction products and thus prevent its further reduction.

Alcohol was the solvent most commonly used in this investigation, but it apparently cannot be used with amines above perhaps 165° because it reacts with them to form secondary or tertiary amines. Methylcyclohexane has proved itself to be an excellent solvent. It is inert and has a good boiling point (100") for easy separation from the reaction products. Ether proved itself of value in that butyl cyanide reduced more rapidly and gave a higher ratio of primary amines to secondary amine when ether was used than in the absence of a solvent. This was even more marked in the case of isonitrosopropiophenone, which reduced faster at 85° in an ether solution than at 125° in methylcyclohexane. The formation of condensation products was much less in ether, but it is not certain whether this was due to the specific influence of ether or to the lower temperature at which it was possible to carry out the reduction. The effect of alcohol in increasing the yield of β-hydroxyethyl butyrate from acetoacetic ester by 50% will he considered in another paper. Water has not been extensively used as a solvent in this work but it did not materially reduce the rate of reduction when it was used with acetone.

There is recorded in the table a summary of the experimental conditions and results obtained in the reduction of a group of representative organic compounds. The fifty experiments whose results are reported have been selected as representative out of a group of approximately 200 experiments devoted to the study of the reduction of these forty-five compounds. There is given in order the number of the experiment according to our laboratory record, the name of the compound reduced, the amount of material (expressed in moles) placed in the reaction vessel, the moles of hydrogen absorbed, the weight and number of the catalyst according to our laboratory records, the volume and kind of solvent, if any, the temperature at which the reaction was carried out, the range of pressure in atmospheres during the reduction, the approximate time required for the absorption of the hydrogen, the name and yield of product(s) expressed in percentages of the theoretical and the observed physical constants as compared with those given in the literature. The yields were calculated in three ways and the method of calculation used in any particular case is indicated by prefixing the letters A, B or C to the figure giving the percentage yield. "A" shows the yield of the compound actually obtained, "B" gives the percentage of the theoretical yield obtained after making an allowance for the mechanical losses. In calculating "C" allowance was made for mechanical losses and also for that part (if any) of the original compound in the reaction mixture which had not been reduced. In almost every case it would be easy materially to increase the "A" yields by using larger quantities of materials and refinements in working up the products. In our opinion the value for the moles of hydrogen absorbed is a better index, in the great majority of cases, of the quantitativeness of the reduction than is the yield given under "A."

TABLE I

SUMMARY OF EXPERIMENTAL RESULTS

Expt.	Compound	Moles	H_2 abs., moles	Catalyst g.	Catalyst No.	Solvent	Solvent ml.	Temp., °C.	Press. range, atm.	Time, hours	Yield, %	Yield, %	Products Compound	Boiling point °C.	Boiling point mm.	Literature Boiling points °C.	Literature Boiling points mm.
187	Acetone	1.0	1.0	2	12	....	...	125	165–15	1.5	A88	B100	Propanol-2	......	...	......	...
10	Pinacolone	0.40	0.38	2	1	....	...	100	127–13	8	A85	C100	Methyl *tert.*-butyl carbinol	115–118	740	117–121[a]	...
175	Acetylbenzoylmethane	.06	.20	2	11	EtOH	50	100	165–15	0.5	A95	...	1-Phenylbutanediol-1,3	167–169	13	162–164[b]	13
162	Acetophenone	.20	..	2	11	EtOH	50	175	160–10	8	...	C60	Methyl phenyl carbinol	202–203	742	203.6[c]	740
231	Ethyl phenyl ketone	.19	..	2	12	EtOH	50	125	170–20	1–2	A85	B100	Phenyl ethyl carbinol	213–215	740	212[d]	...
170	Diacetone alcohol	1.0	1.0	3	11	....	...	150	175–25	2	A93	B100	2-Methylpentanediol-2,4	110–112 195–196	22 740	190–194[e]	740
154	Salicylaldehyde	0.46	0.48	2	9	....	...	100	160–10	1–2	A41	...	*o*-Hydroxybenzyl alcohol	84 (m. p.)		86 (m. p.)[f]	...
103	Cyclopentanone	.50	.49	2	7	....	...	100	130–30	6	A91	B100	Cyclopentanol	137–137.5	...	139[g]	...
45	Cinnamic aldehyde	.40	.76	2	6	....	...	100	92–22	...	A63	...	3-Phenylpropanol-1	118–124	12	120[h]	12
46	Cinnamic aldehyde	.40	.46	2	6	....	...	100	105–15	1	A53	...	3-Phenylpropanal-1	102–106	12	100–105[i]	12
44	Benzaldehyde	.50	.45	2	6	....	...	100	110–10	0.4	A70	...	Benzyl alcohol	......	...	......	...
204	Benzophenone	.10	.11	1	12	EtOH	35	125	160–10	1	A87	...	Diphenyl carbinol	65 (m. p.)	...	65.5–68[j] (m. p.)	...
84	Benzoin	.25	.40	2	6	EtOH	50	125	162–13	1	A90	...	1,2-Diphenyl-ethanediol-1,2	136–136.5 (m. p.)	...	138[k] 134 [l] (m. p.)	...
80	Benzil	.10	.30	2	6	EtOH	65	125	160–10	1	A90	...	1,2-Diphenyl-ethanediol-1,2				
70	Diphenyl carbinol	.17	.20	2	6	....	...	200	180–30	3	A80	B92	Diphenylmethane	......	...	......	...
41	Benzyl alcohol	.48	.52	2	6	....	...	175	75–25	0.5	A75	B95	Toluene	......	...	......	...
180	Benzyl alcohol	.50	.87	2	11	....	...	125	150–25	2	A64	...	Toluene	......	...	......	...
											A23	...	Cyclohexyl carbinol	179–180	740	181[m]	755
63	Benzyl acetate	.33	.36	2	6	....	...	125	175–25	6	...	C100	Toluene	......	...	......	...
131	Trimethylene cyanide	.25	1.05	2	9	Methylcyclohexane	50	150	100–10	3	A33	...	Piperidine	105–106	...	......	...
213	Butyl cyanide	.50	0.98	2	12	....	...	110	100–20	3	A45	B50	*n*-Pentylamine	102–104	740	103–104[n]	...
											A35	B40	Di-*n*-pentylamine	202–203	...	187°; 95–97°	12
217	Butyl cyanide	.50	1.02	2	12	Ether	35	105	175–15	...	A45	B61	*n*-Pentylamine	......	...	......	...
											A30	...	Di-*n*-pentylamine	......	...	......	...
200	*o*-Tolyl cyanide	.35	0.68	2	12	C_7H_{14}	40	125	160–10	1.5	A69	...	*o*-Methylbenzylamine	203–204; 102–105	740 20	199.5[p]	...
256	Phthalimide	.25	.52	2	12	C_7H_{14}	60	200	200–50	4–5	A76	B80	Phthalimidine	151–151.5 (m. p.)	...	150[q] (m. p.)	...
													Phthalimidine picrate	148 (m. p.)	...	140[q] (m. p.)	...
													Nitrosophthalimidine	159 (m. p.)	...	156[q] (m. p.)	...
235	Isonitrosopropiophenone	.025	.08	1	12	Ether	45	85	100–10	1.5	A55	...	1-Phenyl-2-aminopropanol-1	101 (m. p.)	...	103[r] (m. p.)	...
													1-Phenyl-2-aminopropanol-1·HCl	189–191 (m. p.)	...	191[r] (m. p.)	...
152	Benzene	.66	..	2	9	....	...	135	160–10	0.1	A85	B100	Cyclohexane	......	...	......	...
145	Toluene	3.0	..	2	9	....	...	175	175–25	0.3	A96	B100	Methylcyclohexane	99–100	740	100.1[s]	...
164	Ethylbenzene	0.60	1.83	2	11	....	...	175	180–30	1	A93	B100	Ethylcyclohexane	131	740	130[s]	...
166	Butylbenzene	.10	..	2	11	....	...	150	155–15	0.1	...	B100	Butylcyclohexane	178	740	176–177[t]	760

TABLE I (*Concluded*)

Expt.	Compound	Moles	H_2 abs., moles	Catalyst		Solvent		Temp., °C.	Press. range, atm.	Time, hours	Yield,	Products		Boiling point		Literature Boiling points	
				g.	No.		ml.					%	Compound	°C.	mm.	°C.	mm.
227	Diphenyl	0.17	..	2	12	EtOH	60	200	200–40	..	A95	...	Dicyclohexyl	118–120	20	234–236[u] 240–241[v]	745 ...
220	Diphenyl ether	.17	1.20	2	12	....	...	150	160–50	3–4	A42	...	Dicyclohexyl ether	238–239	740	239–240[w]	...
140	Phenol	.50	1.51	2	9	....	...	150	200–50	...	A88	B100	Cyclohexanol[x]	......	...	......	...
122	Hydroquinone	.33	1.10	2	7	EtOH	50	150	170–30	4–6	A88	...	*Cis*-cyclohexanediol-1,4	101–102 (m. p.)	...	102[y] (m. p.)	...
68	2-Phenylethanol	.32	1.09	2	6	....	...	200	155–45	5–6	A66	B75	2-Cyclohexylethanol-1	205–206	740	206–207[z]	740
167	Benzophenone	.20	1.70	2	11	EtOH	100	175	210–60	6	A90	B100	Dicyclohexylmethane	250–251	740	251.5[aa]	760
72	Diphenylmethane	.09	0.58	2	6	EtOH	50	150	175–25	6–7	A83	B91	Dicyclohexylmethane	......	...	......	...
40	Ethyl benzoate	.35	.73	2	6	....	...	150	80–20	7–8	A52	C100	Ethyl hexahydrobenzoate	97–100 198–200	22 745	196.6[bb]	... ...
147	Aniline	1.00	3.07	5	9	C_7H_{14}	100	175	205–55	9	A71	C90	Cyclohexylamine	133.5	740	134[cc]	...
88	Aniline	0.25	0.71	2	7	EtOH	50	200	250–90	...	A91	C95	Ethylcyclohexylamine	162–165	745	164[dd]	...
118	Acetanilide	.25	..	2	7	EtOH	50	175	180–30	6–7	A75	C100	Acetylcyclohexylamine	106–107 (m. p.)	...	107[ee] (m. p.)	...
238	β-Naphthylamine	.14	.20	2	12	C_7H_{14}	35	140	180–20	5	A71	...	*Aci*-tetrahydro-β-naphthylamine	143–147 158–162	15 36	...... 162[ff]	... 36
75	Pyrrole	.75	1.18	2	6	....	...	200	190–40	5–6	A37	C52	Pyrrolidine	88–89	740	87.5–88.5[gg]	...
82	Pyrrole	.50	0.93	2	6	EtOH	50	200	190–40	6–8	A43	...	Pyrrolidine	......	...	......	...
203	Diphenylamine	.17	1.02	2	12	C_7H_{14}	60	175	200–20	3	A73	B95	Dicyclohexylamine	144–145 250–252	30 740	145[cc] 250[cc]	30 750
205	Quinoline	.20	1.03	2	12	....	...	175	175–15	6–8	A95	...	*Cis-trans*-decahydroquinoline	204–206	...	......	...
98	Quinoline	.40	0.72	2	7	....	...	150	160–10	1–4	A88	C96	Tetrahydroquinoline	122–124 244–245	10 745	244–246[hh] 250–255[ii]	725 ...
74	Pyridine	.50	1.45	2	6	....	...	200	175–25	9–11	A80	...	Piperidine	105–106	...	......	...
58	α-Methylpyridine	.50	1.41	2	6	....	...	175	190–30	8–10	A82	B100	α-Methylpiperidine	116–118	...	118–119[jj]	...
144	β-Methylpyridine	.33	..	2	9	C_7H_{14}	25	175	190–40	9–11	A88	...	β-Methylpiperidine	123–127	...	124–126[kk]	...
100	α-Pyridylphenylethylene	.11	0.40	2	7	EtOH	50	150	165–15	...	A82	...	α-(Phenylethyl)-piperidine[ll]	......	...	......	...
188	γ-Pyridylphenylethylene	.11	.47	2	11	EtOH	50	165	175–25	8	A92	...	γ-(Phenylethyl)-piperidine[ll]	......	...	......	...
241	α-Benzylpyridine	.31	1.03	2	12	EtOH	30	160	190–30	7	A85	...	α-Benzylpiperidine[ll]	......	...	......	...

[a] Delacre, *Bull. soc. chim.*, [4] **1**, 455 (1907). [b] Franke and Kohn, *Monatsh.*, **27**, 1115 (1906). [c] Klages and Allendorff, *Ber.*, **31**, 1003 (1898). [d] Wagner, *J. Russ. Phys.-Chem. Soc.*, **16**, 332 (1884). [e] Franke, *Monatsh.*, **27**, 1067 (1902). [f] Lederer, *J. prakt. Chem.*, [2] **50**, 225 (1894). [g] Wislicenus and Hentzschel, *Ann.*, **275**, 322 (1893). [h] Bouveault and Blanc, *Chem. Zentr.*, **II**, 1701 (1905). [i] Bouveault, *Bull. soc. chim.*, [3] **31**, 1332 (1904). [j] Linnemann, *Ann.*, **133**, 9 (1865). [k] Paal, *Ber.*, **16**, 637 (1883). [l] Wislicenus and Blank, *Ann.*, **248**, 5 (1888). [m] Sabatier and Mailhe, *Compt. rend.*, **139**, 343 (1904). [n] Hoffman, *Ber.*, **15**, 770 (1882). [o] Custer, *ibid.*, **12**, 1328 (1879); Rupe, Metzger and Vogler, *Helv. Chim. Acta*, **8**, 848 (1925). [p] Krober, *Ber.*, **23**, 1026 (1890). [q] Graebe, *ibid.*, **17**, 2598 (1884); *Ann.*, **247**, 29 (1888). [r] Hartung and Munch, THIS JOURNAL, **51**, 2262 (1929). [s] Sabatier and Senderens, *Compt. rend.*, **132**, 1255 (1901). [t] Faillebin, *Ann. chim.*, **4**, 421 (1925). [u] Sabatier and Murat, *Compt. rend.*, **154**, 1390 (1912); Borsche and Lange, *Ber.*, **38**, 2769 (1905). [v] Ipatiev, *ibid.*, **40**, 1287 (1907). [w] Schrouth and Wege, *ibid.*, **57**, 858 (1924). [x] *Cf.* Brochet, *Bull. soc. chim.*, [4] **31**, 1270 (1922). [y] Willstätter, *Ber.*, **34**, 507 (1901). [z] Zelinsky, *ibid.*, **41**, 2628 (1908). [aa] Eijkman, *Chem. Weekblad*, **1**, 7 (1903). [bb] Lumsden, *J. Chem. Soc.*, **87**, 92 (1905). [cc] Sabatier and Senderens, *Compt. rend.*, **138**, 457 (1904). [dd] Sabatier and Senderens, *ibid.*, **138**, 1257 (1904). [ee] Skita and co-workers, *Ber.*, **53**, 1242 (1920). [ff] Bamberger and Müller, *ibid.*, **21**, 850 (1888). [gg] Gabriel, *ibid.*, **24**, 3231 (1891). [hh] Hoffmann and Königs, *ibid.*, **16**, 728 (1883). [ii] Ipatiev, *ibid.*, **41**, 992 (1908). [jj] Ladenberg, *Ann.*, **247**, 62 (1888). [kk] Hesekiel and Ladenberg, *ibid.*, **247**, 67 (1888). [ll] Bailey and McElvain, THIS JOURNAL, **52**, 1633 (1930).

The significance, for the present, of the results obtained in the reduction of the majority of the compounds dealt with in this paper lies in the establishment of experimental conditions under which these reductions may be carried out satisfactorily. For this reason and because of the need of economy in the use of space in THIS JOURNAL nothing will be added in most cases to the simple statement of experimental results given above. It should be pointed out, however, that the low yields in the case of the reduction of salicylaldehyde and isonitrosopropiophenone were due to mechanical losses, and in the case of acetophenone to the fact that it contained chlorine which necessitated a higher temperature for reduction with a resultant increase in side reactions. In the case of toluene and benzene the reduction was so rapid that the temperature of the mixture rose 100° above that at which the reduction was being carried out. Two hundred liters (N. T. P.) of hydrogen was absorbed by three moles of toluene within fifteen minutes, by far the larger part being taken up within five minutes.

Cinnamic aldehyde was reduced both to the corresponding saturated aldehyde and to 3-phenylpropanol at 100° by modifying the time of reaction. Von Braun and Kochendorfer, using an undescribed commercial nickel catalyst, obtained large yields of compounds resulting from the condensation of two moles of the aldehyde.[6]

Phthalimide was reduced in a good yield to phthalimidine, the hydrogen absorption being very close to the theoretical. The benzenoid ring was very resistant to reduction, as only small amounts of hexahydropthalimidine were obtained with the nickel catalyst although Willstatter and Jacquet[7] were able to reduce the ring using platinum as a catalyst. Succinimide and succinamide could not be reduced at 200°.

The hydroxyl group of alcohols is, in general, quite resistant to catalytic reduction but if the hydroxyl group is on a carbon atom to which is attached a benzenoid ring, its replacement by hydrogen takes place at 125° or lower. This is shown by the reduction of benzyl alcohol, diphenylcarbinol, triphenylcarbinol and *sym.*-diphenylethylene glycol to the corresponding hydrocarbons. If the hydroxyl group was in the beta position with respect to the ring, the rate of its reduction was retarded very greatly. This same ease of replacement of oxygen by hydrogen when the oxygen is alpha to an unsaturated ring is also met with in the ready reduction of benzyl acetate to toluene and acetic acid and in the rupture of the ether linkage in diphenyl ether when the latter is reduced at 150°. Benzyl alcohol is reduced almost exclusively to toluene at 175° but at 125° the hydrogen is distributed almost equally between alcohol and ring reduction. However, since three moles of hydrogen are required to reduce the ring and only one to reduce the alcohol, the yield of cyclohexylcarbinol is only about one-third that

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[6] Von Braun and Kochendorfer, Ber., 56B, 2172 (1923).

[7] Willstatter and Jacquet, *ibid.*, 51, 767 (1918).

of toluene under the optimum conditions so far discovered. The hydrogenation of the nucleus of aromatic alcohols without the elimination of the hydroxy group has not previously been accomplished.[8] Diphenyl ether reduced readily but the hydrogen absorption was high, due to rupture of the ether linkage, the ratio of straight reduction to reduction with splitting being approximately 2:3. The dicyclohexyl ether obtained boiled at 238–239° as reported by Schrauth and Wege[9] and not at 275–277° as given by Ipatiev.[10]

Aniline absorbed hydrogen more slowly than did the other benzenoid compounds studied. The absorption of hydrogen was almost, if not quite, the theoretical three-mole equivalents, but small amounts of aniline were always found in the reaction mixture. The rate of reduction was rather rapid at first but quickly decreased. Dicyclohexylamine was formed in the ratio of one part of the secondary amine to nine parts of the primary. The actual yield of cyclohexylamine was considerably lowered due to its being carried over with the methylcyclohexane used as a solvent. When alcohol was used as a solvent an excellent yield of ethylcyclohexylamine was obtained. Trimethylene cyanide and butyl cyanide took up the theoretical quantity of hydrogen but a secondary amine was formed to a considerable amount in each case. In fact piperidine was the only product isolated from the reduction of trimethylene cyanide.

The pyridinoid ring in quinoline was rapidly reduced at temperatures from about 125° upward. The tetrahydroquinoline was obtained in practically quantitative yields. The benzenoid ring requires a considerably higher temperature for its reduction but the absorption of hydrogen was that calculated for complete reduction. The product in all experiments had the correct boiling range of 204–206° but in the earlier experiments the product remained a liquid at 0° but on retreatment with nickel and hydrogen it would absorb no additional hydrogen. Bamberger and Lengfeld assign a melting point of 48.2–48.5° to decahydroquinoline while Skita **and** Meyer give 48° and Ipatiev 45.5°. Ipatiev gives a boiling point of 207–210° while the other authors report 204°. Bamberger and Lengfeld report a melting point of 275.5–276° for the hydrochloride. Later, 77 *g.* of quinoline was reduced and 71 g. of product obtained boiling at 204–206°. On cooling to 0°, 42 g. of crystals melting 48–49° was obtained. This is the *trans* isomer. The hydrochloride melted at 278–279°. The liquid has been identified by Mr. C. F. Bailey as the isomeric cis decahydroquinoline described by Hiickel and Stepf,[11] who give an excellent bibliography on the isomeric decahydroquinolines.

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[8] Sabatier–Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Company, New York, 1922, p. 168.

[9] Schrauth and Wege, *Ber.*, **57B,** 859 (1924).

[10] Ipatiev, *ibid.*, 41, 100 (1908).

[11] Hückel and Stepf, *Ann.*, 453, 167 (1927). Bailey and McElvain, THIS JOURNAL, **52,** 4015 (1930).

Nickel has been considered to be inferior to platinum as a catalyst for hydrogenation because, in general, nickel is not active as a catalyst at room temperature. This characteristic has its advantages, however, as it permits selective reduction between two reducible groups through control of temperature of hydrogenation, Such selective reduction was achieved at 125° with acetylbenzoylmethane, phenyl ethyl ketone, benzoin, benzil, benzophenone, isonitrosopropiophenone, benzyl cyanide and *o*-methyl phenyl cyanide when the carbonyl, oxime or cyanide group was reduced without affecting the benzenoid ring. At 175 to 200° complete reduction of these compounds occurred. By a similar temperature control it was found possible to reduce the pyridinoid ring in quinoline, α-pyridylphenylethylene, γ-pyridylphenylethylene and a-benzylpyridine without reducing the benzenoid ring.

Summary

The preparation of a reasonably active nickel catalyst has been described and experimental details are given for the satisfactory reduction of forty-five representative organic compounds. The results have been summarized and need not be repeated here. In general, it may be said that an apparatus and technique have been used which have made it possible to determine rather accurately the amount of hydrogen absorbed and the rate of the reduction. This has made it feasible readily to carry on selective reduction of one of two reducible structures through the control of the temperature or time interval of the reduction. The merits of methylcyclohexane, alcohol and ether as solvents during reduction have been discussed.

MADISON. WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF THE UNIVERSITY OF BUFFALO]

THE KETO-ENOL EQUILIBRIUM OF ETHYL ALPHA-PHENYL ACETOACETATE

BY HOWARD W. POST AND GLADYS A. MICHALEK[1]

RECEIVED JUNE 6, 1930 PUBLISHED NOVEMBER 5, 1930

The keto-enol equilibrium of ethyl acetoacetate and its derivatives has already received considerable attention, most of the data published being concerned with the unsubstituted ester or its alkyl derivatives. The effect of substituents in the a-position, especially phenyl, has not been extensively investigated as far as the keto-enol equilibrium of the compounds is concerned. It was our purpose to prepare ethyl α-phenyl acetoacetate and to study its keto-enol equilibrium by means of bromine titration as well as its index of refraction.

[1] Presented to the Committee on Graduate Study of the University of Buffalo by the second author in partial fulfilment of the requirements for the degree of Master of Art..

At ordinary temperatures pure ethyl acetoacetate exists in the enol form to the extent of about 7.7% while α-methyl acetoacetic ester contains about 4.1% enol (at 18°). α,γ-diphenyl acetoacetic ester contains about 18.5% enol at 100°.[2]

Ethyl thiolacetoacetate shows 30.8% enol.[3]

The enol form may be titrated against standard bromine solution[4] or we may depend on some physical property such as refractive index.[5]

The n^{20}_{D} of ethyl acetoacetate has been found to be 32.000, corresponding to 59.2% enol at 20°. Obviously this is at wide variance with the value 7.7% obtained by bromine titration and it was our intention to investigate the composition of equilibrium mixtures of ethyl α-phenyl acetoacetate as evidenced by the figures on enol content obtained both by bromine titration and by the determination of the refractive index.

We prepared ethyl α-phenyl acetoacetate by the method of Beckh, modifying the procedure, however, to increase the yield, which was none too great even then, Enol content was determined by bromine titration (indirect method) and by the determination of the molecular refraction.

Preparation of the Ester.—a-Phenyl substitution products of acetoacetic ester may be made by treating the sodium derivative of ethyl acetoacetate with the proper aryl halide providing there are substituents in the ring to give the halogen the necessary negativity. The indirect method of Beckh,[6] however, had to be resorted to in the preparation of the phenyl derivative, modified as follows.

Benzyl cyanide and ethyl acetate were condensed in the presence of sodium ethylate to give the sodium derivative of acetobenzyl cyanide. This nitrile was then hydrolyzed to the ester by means of hydrochloric acid and ethyl alcohol, through the stage of the imide of the ester.

Our procedure differed from that of Beckh in several particulars. In the first place, instead of dissolving the sodium in absolute alcohol, it was suspended in dry ether and the alcohol added. This was merely for the sake of convenience. Second, after condensation of the ethyl acetate and benzyl cyanide, Beckh removed unchanged benzyl cyanide by dissolving the salt in water and extracting with ether. We found it somewhat more effective and considerably more convenient to wash the salt with ether before dissolving in water. After freeing the acetobenzyl cyanide with carbon dioxide, Beckh extracted it with ether. At the comparatively low temperature which was obtained by using a strong stream of carbon dioxide from a tank, the acetobenzyl cyanide came down as crystals which could be removed by filtration. This gave a somewhat purer product than would have been obtained by extraction. Our greatest deviation, however, from the method of Beckh lay in the decomposition of the imido ester. We poured the alcohol solution directly into ice water, extracted with ether, washed the ether solution directly into ice water, and washed the ether solution with sodium carbonate solution, while Beckh allowed the alcoholic solution to stand over potassium hydroxide or soda lime for several days.

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[2] Dieckmann, *Ber.*, 55B, 2470 (1923).

[3] Baker and Reid, THIS JOURNAL, 51, 1567 (1929).

[4] Meyer, *Ann.*, 380, 212; Grossmann, *Z. physik. Chem.*, 109, 305 (1924).

[5] Auwers, *Ber.*, 44, 2523 (1911).

[6] Beckh. *ibid.*, 31, 3160 (1898).

Allowing the mixture to stand over soda lime or potassium hydroxide did not remove all the hydrochloric acid even when a considerably longer time than directed was allowed. In one run we attempted to remove it by blowing dry air through the solution held at about 40°. Before all the acid was removed the solution began to precipitate and on completing the hydrolysis we recovered the acetobenzyl cyanide almost quantitatively.

The yields were never high. In the condensation between ethyl acetate and benzyl cyanide the yield was between 25 and 30% of the theoretical. About 25% of the benzyl cyanide could be recovered. In the hydrolysis of the acetobenzyl cyanide the purified ester never represented more than 10% of the theoretical amount and often as low as five.

Acetobenzyl cyanide crystallized in glistening white crystals melting at 90°; insoluble in water, easily soluble in alcohol, ether and ethyl acetate. The alcoholic solution gave a weak green color with ferric chloride. It is also soluble in sodium carbonate solution and other alkaline media, from which it can be precipitated by acidification. It absorbs bromine readily.

Ethyl α-phenyl acetoacetate is a colorless, slightly viscous oil boiling at 145–147° at 11-mm. pressure. Its alcoholic solution gives a strong violet color with ferric chloride solution.

Anal. Calcd.: C, 68.86; H, 6.84. Found: C, 68.66, 68.56; H, 6.66, 6.50.

The phenylhydrazone of ethyl u-phenylacetoacetate was prepared by heating the ester with phenylhydrazine. It crystallizes in white needles turning yellow on exposure to the air; melting point, 103.9 to 104.2°, Beckh reporting 104°.

1,4-Diphenyl-3-methyl-5-pyrazolone was prepared by heating the hydrazone to 170°, whereupon it melted and then solidified, forming crystals which when recrystallized from acetic acid melted at 193–195°. Beckh reported this melting point as 196'.

Bromine Titration

In titrating the enol form of ethyl α-phenyl acetoacetate against standard bromine solution, we first compared what are known as the direct and the indirect methods. By the direct method[7] the alcohol was cooled to −7°, the ester dissolved therein quickly and titrated against freshly prepared bromine ($N/5$). Since the alcoholic bromine solution is not stable for any great length of time, it must be standardized at the time of use. By the indirect method[8] the sample is dissolved in alcohol as before and alcoholic bromine added. The bromine is here approximately of $N/5$ strength and is added until a faint yellow color persists. The excess is then removed by the addition of 2 cc. of alcoholic β-naphthol solution. Potassium iodide solution is then added and the solution heated generally for twenty minutes on the water-bath in the dark, the liberated iodine being titrated against sodium thiosulfate solution. Trying both methods we found the volumes of thiosulfate and bromine to check.

Number	1	2	3
Bromine, cc.	4.60	5.05	5.45
Direct, $Na_2S_2O_3$ equiv., cc.	7.2	8.45	8.45
Indirect, $Na_2S_2O_3$, cc.	7.15	8.3	8.45

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[7] Auwers and Eisenlohr, Z. *physik. Chem.*, 83, 429 (1913).

[8] Meyer, *Ber.*, 44,2718 (1911).

Using the indirect method of Meyer we obtained the following values for ethyl α-phenyl acetoacetate

Sample, g.	0.4223	0.3317	0.3012	
$Na_2S_2O_3$, cc.	10.8	8.7	7.9	
Enol, %	27.9	28.9	28.9	**Av.,** 28.6

The literature seems to agree that the amount of thiosulfate used is directly proportional to the amount of bromine absorbed. We suggest, as a mechanism, the splitting off of positive bromine, its reaction with potassium iodide to liberate 2I and the reaction of the 21 with sodium thiosulfate. Obviously it would be rather difficult to prove this—isolation of bromo ester undoubtedly would not give us positive bromine united to carbon for very long—a shift to negative bromine would be expected to take place almost immediately when isolated.

Molecular Refraction

Using the additive values found in the literature for the various elements in ethyl acetoacetate and applying these values to the α-phenyl ester, including modifications for various constructions, we calculated the molecular refraction for the equilibrium mixture as follows

$$n_D^{20} = 1.5130 \text{ and } d_4^{20} = 10850$$

Then using the formula

$$\frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d} = 57.10$$

The data for ethyl acetoacetate compared with those for ethyl α-phenylacetoacetate can be plotted as follows

	100% keto calcd.	Found	100% enol
$CH_3COCH_2COOC_2H_5$	31.57	32.00	32.62
$CH_3COCH(C_6H_5)COOC_2H_5$	55.66	57.10	56.71

using Brühl refraction equivalents.[9]

From these figures it will be seen that ethyl acetoacetate shows an enol content of 59.2% by the method of the refractive index and ethyl α-phenyl acetoacetate, 137.13%. These results are nowhere near the values obtained by bromine titration, 7.7 and 28.6%, respectively, and under the circumstances we prefer to place more reliance on the latter pair of figures, as indeed do all those who have preceded us in this sort of work.

We explain our "abnormal" results by assuming an effect due to the presence of the phenyl group in the a-position. We have here at least one pair of conjugate double bonds and if we do not wish to pin ourselves down to any structure of benzene, at least we have the anomalous structure of the phenyl radical, whatever its actual configuration, to use as a reason for this increase in molecular refraction over the value calculated additively. Other investigators have met with the same obstacles.

[9] Brühl, *Ber.*, **27**, 2478 (1894).

Discussion of Results

Ethyl α-phenyl acetoacetate has been found to contain 28.6% of the enol form at room temperatures (20°) in pyrex glass. This is higher than that of the unsubstituted ester and the methyl derivative. These and other values mostly taken from the literature are as follows

$(CH_3CO)_2CHCOOC_2H_5$	100% enol
$CH_3COCH(C_6H_5)COOC_2H_5$	28.6% enol
$CH_3COCH_2COOC_2H_5$	7.7% enol
$CH_3COCH(CH_3)COOC_2H_5$	4.1% enol
$CH_3COCH(CH_2C_6H_5)COOC_2H_5$	3.4% enol
$CH_3COCH(C_2H_5)COOC_2H_5$	Mostly ketonic
$CH_3COCH(CH_2—CHCH_2)COOC_2H_5$	Mostly ketonic

From data at hand, then, it would appear that electropositive substituents repress enolization or at least are accompanied by such repression and electronegative groups facilitate this process.

Conclusions

Lowry and Burgess propose the chelate ring formula for acetoacetic ester.[10] If we modify this conception to admit of oscillation of affinity to account for keto and enol shift, the effect of an electronegative group, substituted in the α-position is more apparent. This group facilitates ionization of the a-hydrogen in much the same manner that chlorine is said to facilitate ionization of the substituted acetic acids.

Materials.—Benzyl cyanide was obtained from the Eastman Kodak Co., and used as received. That recovered from the acetobenzyl cyanide synthesis was washed with water, dried over calcium chloride and distilled under reduced pressure.

Ethyl acetate was washed with dilute alkali, then several times with water and dried over calcium chloride or anhydrous copper sulfate. It was then separated and distilled.

Hydrochloric acid gas was generated by dropping concentrated sulfuric acid on dry sodium chloride.

Summary

1. A method for the preparation of a-phenyl acetoacetic ester is outlined. This method is a modification of one already in the literature.
2. Reliable data from bromine titration of this ester show that it has an enol content at equilibrium, room temperature, in pyrex glass, of 28.6%. A mechanism is suggested for this series of reactions.
3. Data on the enol content obtained from a determination of the molecular refraction show 137.13%, obviously unreliable.
4. The increase in enol content of the a-phenyl ester over that of the unsubstituted ester is ascribed to the greater electronegativity of the phenyl over hydrogen, and the abnormally large value obtained by the refractive index method, to the presence of the anomalous benzene ring.

BUFFALO. NEW YORK

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[10] Lowry and Burgess, *J. Chem. Soc.*, 123,2111 (1923).

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

NOTE ON THE PURIFICATION OF PHENANTHRENE[1]

BY FRANK L. COHEN AND ULYSSE CORMIER

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Crude phenanthrene from anthracene oil is obtainable as a dark brown oily crystalline substance. It consists largely of phenanthrene, with varying amounts of anthracene, fluorene, carbazole and dark tarry substances. Of these, anthracene is the most persistent, and its complete removal offers considerable difficulty. By fractional crystallization from a number of solvents, a nearly white product can be obtained which, however, melts variously from 102 to 115°, and gives a brilliant red picrate (phenanthrene picrate is pure yellow, with no red tinge).

The toluene method of Wense[2] involves great losses of material, and does not give a sufficiently pure product, nor did Schmidt's procedure[3] give any better results; the method of Anschiitz and Schultz[3,4] is difficult to carry out on large quantities of material. The alkali fusion method[6] is likewise poorly adapted to laboratory use. Purification over the picrate[6] also proved impracticable and too expensive on a large scale. The red picrate from the partially purified phenanthrene, when recrystallized many times and boiled with prepared charcoal, is obtained as yellow hair-like needles of m. p. 145°, but on decomposition with ammonia always gives phenanthrene melting at about 102 to 105°.

As emphasized by Anschütz,[4] phenanthrene is far easier to separate from anthraquinone than from anthracene itself; we therefore turned to a method used by Sandquist,[7] in which the novel feature was a controlled oxidation with concd. nitric acid. Under the conditions employed, anthracene is oxidized to anthraquinone almost completely, while the phenanthrene is nitrated only to a negligible extent. Sandquist made use of the picrate as well, which we have found to be time-consuming and expensive. Over forty kilograms of phenanthrene has been purified in this Laboratory by the method described below; it is rapid, economical, and can be applied to any reasonable quantity of material. The product is obtained in nacreous white flakes of m. p. 99–99.5°, and gives a pure yellow picrate (compare Limpricht, Ref. 6) of m. p. 145°.

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[1] This work was supported by the Committee on Drug Addiction of the National Research Council.

[2] Wense, *Ber.*, 19, 761, note 3 (1886).

[3] Schmidt, *ibid.*, 12, 1159 (1879).

[4] Anschütz and Schultz, *Ann.*, 196, 32 (1879).

[5] Akt. Teer- u. Erd-Oel Ind., German Patent 130,679.

[6] Limpricht, *Ber.*, 6, 532 (1873).

[7] Sandquist, "Studien über die Phenanthrensulfosäuren," Dissertation, Upsala, 1912.

Experimental

Five kg. of crude phenanthrene was refluxed with 12 liters of 95% alcohol until solution was complete. This was cooled to about 15° and filtered; the use of a basket centrifuge at this point proved to be of great advantage, both in the amount of solvent recovered and in increased purity of the product. From 4.0 to 4.3 kg. of gray crystalline material of m. p. 105–110° was obtained.[8] This crystallization removed the oily and wax-like impurities and most of the color. A small amount of phenanthrene goes with the mother liquor, but is so impure that its recovery is unprofitable.

The purified product so obtained is now further treated in smaller lots. One kilogram was dissolved in 6 liters of alcohol, 120 g. of concd. nitric acid added and the solution refluxed vigorously for one and a quarter to one and a half hours. If any considerable quantity of red product separates from the hot reaction mixture at this point, it should be filtered out of the nearly boiling solution (centrifuge). When cooled, the solution set to a mass of large red flakes, yield 800 to 900 g., m. p. 93–96°.

The substance was now distilled at atmospheric pressure, using about 500 g. in a liter distilling flask provided with a wide arm about 60 cm. in length to serve as an air condenser. The phenanthrene distilled as a pale yellow oil and dropped from the side arm into a large beaker of water which was stirred mechanically. The distillate solidified in thin yellow flakes or shells. Distillation was continued until the liquid began to come over somewhat darkened. Further heating results in a violent explosion; there is no danger of explosion if the distillation is interrupted at the point where the dark distillate begins to come over. Distillation at reduced pressure is impracticable because of clogging of the delivery tube with crystals.

The dried flakes of the distillate were recrystallized from alcohol (4 to 4.5 kg. in 12 liters), again centrifuging for best results. A second recrystallization may be necessary to obtain a pure white product. Crude phenanthrene varies greatly, and in two cases a second oxidation with nitric acid was found necessary. The yield of pure phenanthrene of m. p. 99–99.5° was from 30–45% of the weight of crude starting material. Over 80% of the solvent can be recovered when the centrifuge is used.

UNIVERSITY, VIRGINIA

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[8] The presence of more than about 2% anthracene in phenanthrene raises the melting point, as may be shown by direct experiment.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

MIXED CATALYSTS IN THE FRIEDEL AND CRAFTS REACTION. THE YIELD OF BENZOPHENONE FROM BENZOYL CHLORIDE AND BENZENE USING FERRIC CHLORIDE–ALUMINUM CHLORIDE MIXTURES AS CATALYSTS

BY W. A. RIDDELL AND C. R. NOLLER

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Those who have used the Friedel and Crafts reaction to any extent are familiar with the fact that the yield of product may vary when different lots of the commercial grades of aluminum chloride are used. The usual explanation is that this variation is caused by exposure of the catalyst to moisture. Another possibility, however, is that the variation is due to a positive or negative acceleration of the main reaction or of side reactions, or the inauguration of side reactions by impurities. Ordinary aluminum is about 98 to 99% pure, the impurities being chiefly iron and silicon,[1] and hence aluminum chloride prepared from it would be expected to contain these same impurities. Aluminum chloride prepared from bauxite[2] would contain a considerably higher percentage of impurities than that made from aluminum.

In view of the well-known effect of impurities on many catalytic reactions, it seemed that an investigation of the effect of impurities in the catalyst on the yield of products from various Friedel and Crafts reactions would be desirable. Since ferric chloride alone is known to have considerable activity[3] and is also known to be an impurity of aluminum chloride, an investigation of the use of mixtures of ferric chloride with aluminum chloride was undertaken. Since we began this work, we have become aware of a publication along similar lines[4] and feel that it is desirable to publish our results in so far as they are complete at the present time.

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[1] The following analysis of three samples of aluminum is given by Calvet, *Compt. rend.,* **188,** 1111 (1929).

	Iron	Silicon	*Copper*	**Aluminum by diff.**
Aluminum prepared by Hoopes process	0.015	0.019	0.022	99.944
Pure aluminum	0.16	0.09	nil	99.75
Ordinary aluminum	0.46	0.36[a]	nil	99.18

[a] The value 0.036 is given but this must be a typographical error.

[2] McAfee, *Ind.* Eng. *Chem.,* **21,** 670 (1929).

[3] Nencki and co-workers, ***Ber.,*** 30, 1766, 1768 (1897); 32, 2414, 2419 (1899).

[4] Boswell and McLaughlin, *Can.* J. *Res.,* **1,** 400 (1929); *C.* **A., 24,** 834 **(1930).** These investigators measured the amount of hydrogen chloride evolved in the reaction of benzene with chloroform. The catalysts used were aluminum chloride prepared from ordinary aluminum in various ways, ferric chloride, partially reduced ferric chloride and two mixtures of ferric chloride and aluminum chloride. Evidence is given for a maximum activity when an equimolecular mixture of ferric chloride and aluminum chloride is used.

After several preliminary experiments, it was decided to study first the reaction between benzoyl chloride and benzene. This reaction is not strictly catalytic since the optimum yields are obtained when one mole of aluminum chloride is used per mole of acid chloride. The reasons for studying this reaction, however, were that a comparison of the behavior of the catalysts could be based on the actual yield of the main product of the reaction, and that the results could be duplicated within an experimental error of 2 to 4%. Moreover, in this particular case the catalyst is completely in solution at the end of the reaction so that one is dealing essentially with a single phase system.

Pure aluminum chloride was obtained by the action of chlorine on aluminum having a purity of 99.95%.[5] The material obtained in this way was practically white as contrasted with the gray to deep yellow color encountered in the commercial grades of aluminum chloride. The anhydrous ferric chloride used was a commercial product that was resublimed in a current of nitrogen just before use. In each case where mixtures of aluminum chloride and ferric chloride were used, a homogeneous catalyst was obtained by fusing the mixture in a sealed tube. Actually it appears that the same results are obtained if a simple mixture of the powdered chlorides is used. The exact method of carrying out the reaction is given in the experimental part.

The first series of reactions was carried out to determine the effect of varying the molecular ratio of aluminum chloride to benzoyl chloride. Although it is generally recognized that, in the preparation of ketones, one mole of aluminum chloride is required for each mole of acid chloride,[6] no comprehensive data have been recorded on this point. The results obtained are plotted in Curve I, Fig. 1. According to the procedure used, there was a small amount of material obtained when benzene and benzoyl chloride alone were present, so that the curve does not pass exactly through the origin. As the amount of aluminum chloride is increased, the yield of benzophenone increases in direct proportion[7] until slightly over one mole of aluminum chloride is present. Further increases in the amount of aluminum chloride have no effect.

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[5] The authors are indebted to the Aluminum Company of America for supplying them with aluminum prepared by the Hoopes process and having this high degree of purity. Aluminum chloride was also prepared by passing carbon tetrachloride vapor over pure alumina heated to redness, but this method is much slower and more difficult. Moreover, the product obtained was not quite as pure as that made from pure aluminum.

[6] Rubidge and Qua, THIS JOURNAL, 36, 732 (1914).

[7] Considerable trouble was experienced in obtaining concordant results when less than 0.5 mole of aluminum chloride was used. This was caused by the difficulty of removing completely the unreacted benzoyl chloride when it was present in considerable quantity, and was overcome by treating the benzene solution with an aqueous alcoholic solution of sodium hydroxide.

The second series was carried out on mixtures of aluminum chloride and ferric chloride. The total amount of mixed chlorides was kept constant at 1.1 moles and the composition varied from 100% ferric chloride to 100% aluminum chloride. The results are plotted in Curve II, Fig. 1, and indicate that in this reaction the use of mixtures gives results that are practically the mean between those obtained with pure aluminum chloride and pure ferric chloride.

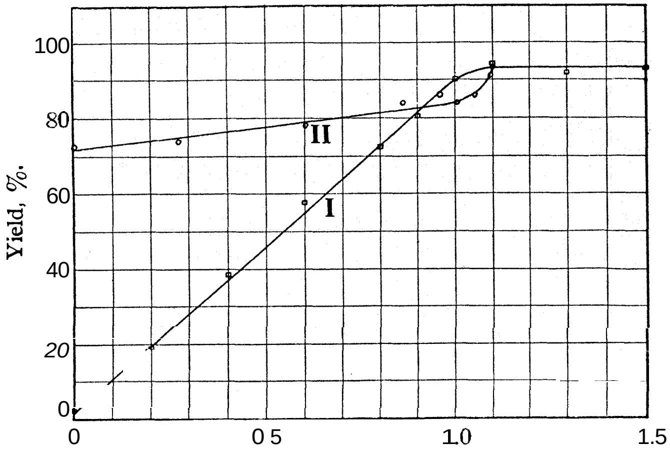


Fig. 1.—Curve I, variation of yield with amount of $AlCl_3$; Curve II, variation of yield using mixtures of $FeCl_3$ and $AlCl_3$, and keeping the total amount of catalyst at 1.1 moles per mole of C_6H_5COCl.

Apparently the lower yields when ferric chloride is present are caused by the acceleration or inauguration of a side reaction. Thus in all cases where ferric chloride is used, a by-product containing iron is formed which is insoluble in the reaction mixture. Further evidence of this detrimental effect is shown by Curve II, Fig. 2. In this series of reactions the amount of aluminum chloride was maintained constant at 1.1 moles, and additional ferric chloride added. In order to compare these results with those obtained when ferric chloride replaces aluminum chloride, the latter have been replotted as Curve I, Fig. 2. Curve II approximates Curve I at first but soon drops below it. A possible explanation of this fact is that when sufficient aluminum chloride is present to take care of all the needs of the main reaction, a greater amount of the ferric chloride is available for producing the side reaction. This explanation would also account for the initial rapid drop of Curve II, Fig. 1, with increasing amounts of ferric chloride. As long as ferric chloride replaces aluminum chloride that is in excess of one mole, the effect is very pronounced, but as the amount of aluminum chloride drops below one mole, the curve flattens out to a straight line whose slope is less because more of the ferric chloride is being used for the main reaction and less is available for producing the side reaction.

The yields of benzophenone are so high that no difference can be detected between the use of pure aluminum chloride and of resublimed commercial products. Some evidence has been obtained in another reaction, however, which indicates that the action of ferric chloride may be different in different types of the Friedel and Crafts reaction.

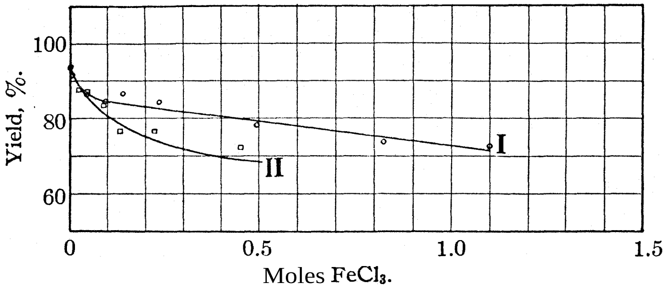


Fig. 2.—Curve I, same as Curve II, Fig. 1, replotted; Curve II, variation of yield using 1.1 moles $AlCl_3$ + varying amounts of $FeCl_3$.

Experimental

Reagents.—Pure anhydrous aluminum chloride was prepared in a suitable apparatus by passing chlorine over heated coils of aluminum sheet having a purity of 99.95%,[5] and was resublimed in an atmosphere of dry nitrogen just before use. The product obtained in this way was almost white, showing only the faintest yellow color in large crystals.

The anhydrous ferric chloride was a commercial C. P. grade and was resublimed in a current of dry nitrogen. Because of the rapid absorption of moisture from the atmosphere, it was necessary to work very rapidly with this material.

A commercial grade of benzoyl chloride was used which boiled at 196–198° and melted at −1 to 0°.

The benzene was dried by distillation and collected over a boiling range of less than 1°.

General Procedure.—Homogeneous mixtures of aluminum chloride and ferric chloride were prepared by placing the two salts in the desired proportions in a pyrex tube, sealing and heating in a bomb furnace until fused. The furnace was tilted at an angle so that the liquid collected in the lower end of the tube.

A 500-cc. three-necked, round-bottomed flask was fitted with a sealed mechanical stirrer, a dropping funnel and a reflux condenser carrying an exit tube for leading off the hydrogen chloride evolved during the reaction. The powdered catalyst was rapidly weighed and transferred to the flask, which contained 70 cc. of dry benzene. After starting the stirrer, 24 g. (0.17 mole) of benzoyl chloride was run in as rapidly as possible. After the reaction had slowed down somewhat, the mixture was refluxed with stirring for three and one-half hours, after which time the evolution of hydrogen chloride had stopped. After cooling, the contents of the flask was decomposed by pouring into 250 cc. of cold water, 10 cc. of concd. hydrochloric acid was added, and the two layers separated. The benzene layer was washed three times with 50-cc. portions of 10% hydrochloric acid and this followed by three washings with 50-cc. portions of 10% sodium hydroxide and a final washing with water. The various aqueous layers were washed successively with a 50-cc. portion of benzene and this was added to the main benzene solution. In the first four runs plotted in Curve I, Fig. 1, where a considerable excess of benzoyl chloride remained at the end of the reaction, it was necessary to modify the method of purifying the benzene solution. It was found that even hot dilute sodium hydroxide would remove the benzoyl chloride only very slowly. This difficulty was overcome by treating the benzene solution, after washing with hydrochloric acid, with 75 cc. of an aqueous alcoholic solution of sodium hydroxide prepared by adding an equal volume of 95% alcohol to a 12N solution of sodium hydroxide. It is essential that a decided excess of sodium hydroxide be present to prevent the formation of ethyl benzoate.

The purified benzene solution was dried over calcium chloride, the benzene distilled, and the residual oil heated in *vacuo* to 160° (thermometer in liquid) at 25-mm. pressure. The resulting crude benzophenone was weighed for yield.[8] The results are plotted in Figs. 1 and 2.

Summary

1. The yield of benzophenone prepared by the reaction of benzoyl chloride with benzene in the presence of mixtures of ferric chloride and aluminum chloride, has been found to be approximately the mean of that obtained using pure ferric chloride and pure aluminum chloride.

2. The ferric chloride has a detrimental action which is apparently due to the acceleration or inauguration of an unknown side reaction.

STANFORD UNIVERSITY, CALIFORNIA

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

THE MERCURATION OF BETA-RESORCYLIC ACID

BY REUBEN B. SANDIN AND JACOB M. ZEAVIN

RECEIVED JUNE 18, 1930 PUBLISHED NOVEMBER 5, 1930

During the course of a study of the mercuration of resorcinol and some resorcinol derivatives,[1] it was decided to mercurate a carboxylic acid derivative of resorcinol. β-Resorcylic acid was selected for this work, because of the three carboxylic acid derivatives of resorcinol it is probably the easiest to prepare.

It has been found that β-resorcylic acid very readily forms monomercurated and dimercurated derivatives. The compounds produced are somewhat similar in properties to the corresponding mercurated alkyl resorcinols.[1] The reactions involved are also similar. The β-resorcylic acid derivatives, however, seem to form more stable compounds. For instance, they do not darken appreciably when exposed to sunlight. Also they are

[8] The yields were more readily duplicated using this procedure than by calculating the yield on the distilled product. On distillation practically the entire amount came over between 184 and 186° at 25 mm.

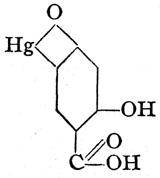
[1] Sandin, THIS JOURNAL, 51, 479 (1929).

more soluble in alkali solutions and these solutions are more stable than the alkali solutions of the mercurated alkyl resorcinols.

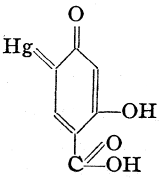
Very recently Fox and Whitmore[2] have found that certain organic compounds can be mercurated in alkaline solution, while other compounds of similar structure cannot. In this work it has been found that β-resorcylic acid is readily mercurated in alkaline solution.

The authors have noticed, as was also the case in the previous work on resorcinol compounds, that a yellow to brown color is associated with the mercurated derivatives which presumably have an anhydro structure. For that reason it is suggested that an alternative structure which involves a quinoid grouping might be used. (Compare formulas I and II. There is no evidence in this work that the substance corresponding to formula II may not be of a para quinoid form instead of the ortho.)

I



II



The mercurated derivatives described cannot be purified by crystallization. They readily lose acetate groups and form anhydro groups, especially on the application of heat. For these reasons, in order to prepare compounds of definite and constant mercury content, the experimental conditions must be constant and rigidly followed. The starting materials must also be quite pure.

Experimental Part

Anhydro-5-hydroxymercuri-β-resorcylic Acid.—The β-resorcylic acid used in this preparation and in subsequent work was obtained from the Eastman Kodak Co. Some β-resorcylic acid was also prepared for this work by the action of potassium bicarbonate on resorcinol.[3] Three and eight-tenths g. (0.02 mole).[4] of β-resorcylic acid dissolved in about 25 cc. of hot glacial acetic acid was added to a hot solution of 3.18 g. (0.01 mole) of mercuric acetate in 25 cc. of glacial acetic acid. The resulting solution was heated for a few minutes and then poured into about one liter of cold water. It was allowed to stand for twelve hours. The white solid (probably the monohydroxymercuri-β-resorcylic acid) was filtered off, washed with water and then dried in the air oven at 100° for twelve to twenty-four hours. It became slightly colored. There was probably the loss of water to form the anhydro-5-hydroxymercuri-β-resorcylic acid. The yield was 95%. It is soluble in a solution of sodium hydroxide.

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[2] Fox and Whitmore, THIS JOURNAL, 51, 2196 (1929).

[3] Nierenstein and Clibbens, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1930, Vol. X, p. 94.

[4] The above quantity and also the calculation of the percentage yields of mercurated derivatives are based upon the assumption that the β-resorcylic acid is anhydrous.

Anal. Calcd. for $C_7H_4O_4Hg$: Hg, 56.9; acetic acid, 0. Found: Hg, 56.8, 56.7, 57.1, 56.3; acetic acid, 0.[5]

The probable structure of this compound is indicated by formula I or II.

In order to prove the position of the mercury group, one molecular proportion of iodine was added to a suspension of one molecular proportion of the monomercurated compound in glacial acetic acid. This mixture was allowed to stand for about twelve hours, with occasional warming and stirring. The filtrate from this mixture was diluted with water, the precipitate filtered off and extracted with alcoholic alkali. The mono-iodo acid was recovered from the extract by dilution with water and acidification. The product melted at 172° without further purification. Nicolrt and Sampey[6] give 172" as the melting point of 5-iodo-2,4-dihydroxybenzoic acid.

Anhydro-3-hydroxymercuri-5-acetoxymercuri-β-resorcylic Acid. Thrco and eight-tenths g. (0.02 mole) of @-resorcylicacid dissolved in 50 cc. of hot alcohol was added to a boiling solution of 12.72 g. (0.04 mole) of mercuric acetate in 300 cc. of alcohol and 5 cc. of glacial acetic acid. Almost instantly a pale yellow solid separated. It was immediately filtered off by suction and washed with hot alcohol. It was air dried for three days. The yield was 11.6 g. or 95%. It is soluble in a solution of sodium hydroxide, but otherwise insoluble in the ordinary organic solvents.

Anal. Calcd. for $C_9H_6O_6Hg_2$: Hg, 65.6; acetic acid, 9.8. Found: Hg, 64.8, 64.8; acetic acid, 9.1. Other preparations of this compound gave the following percentages for mercury: 66.4, 66.1, 65.6, 65.5.

Of the several attempts to replace the mercury groups by iodine, according to the procedure outlined above, only one was apparently successful. The di-iodo acid obtained decomposed at 191–195°.

Nicolet and Sampey[6] give the decomposition range of 3,5-di-iodo-2,4-dihydroxybenzoic acid as 193–196°.

In the preparation of the above dimercurated derivative, if a large amount of glacial acetic acid was used and practically no alcohol, or if the experiment as already described was carried out and then followed by a heating on the water-bath, a precipitate which was white and not yellow was obtained. This compound was probably the **di-acetoxymercuri-β-resorcylic** acid. However, attempts to obtain it pure by using glacial acetic acid as the medium were unsuccessful. The material on drying gradually lost acetic acid and became colored. The mercury content at the same time gradually approached that required for the **anhydro-3-hydroxymercuri-5-acetoxymercuri-β-resorcylic** acid.

Mercuration of **β-Resorcylic** Acid in Alkaline **Solution.**—β Resorcylic acid was converted into a dimercurated derivative, in alkaline solution according to the procedure of Fox and Whitmore.[2] The mercurated compound was precipitated by bubbling carbon dioxide through the alkaline solution or by nearly neutralizing the solution with dilute hydrochloric acid. The compound, which was brown in color, was probably anhydro-3,5-dihydroxymercuri-β-resorcylic acid. The yield was 80%.

Anal. Calcd. for $C_7H_4O_5Hg_2$: Hg, 70.4. Found: Hg, 69.9, 69.4, 69.3, 71.4.

Summary

1. The mercuration of β-resorcylic acid gives mono and dimercurated products.

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[5] It was evident that the carbon dioxide formed by the decomposition of the β-resorcylic acid [Hemmelmayr and Meyer, *Monatsh.*, 46, 143 (1916)] would interfere with the titration of acetic acid by the regular method [White, THIS JOURNAL, 42, **2355** (1920)]. For this reason a blank determination was carried out on β-resorcylic acid and phosphoric acid, making conditions as similar to the actual determinations as possible.

[6] Nicolet and Sampey, THIS JOURNAL, 49. 1796 (1927).

2. The anhydro compounds obtained are colored in such a way as to indicate the possibility of quinoid structure.
3. β-Resorcylic acid can be mercurated in alkaline solution to give a dimercurated product.

EDMONTON, ALBERTA, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

THE THERMAL DECOMPOSITION OF GASEOUS GERMANIUM TETRAETHYL

BY RAY L. GEDDES[1] AND EDWARD MACK, JR.

RECEIVED JUNE 24, 1930 PUBLISHED NOVEMBER 5, 1930

In connection with the modern theory of the mechanism of gaseous reactions it probably would be very helpful to study the kinetics of decomposition of a series of molecules which present a stepwise gradation of structure and stability. With this in mind we have begun an investigation of the thermal decompositions of the tetra-alkyls (such as the tetramethyls and tetraethyls) of carbon, silicon, germanium, tin and lead. This family of compounds presents a considerable variety of sizes of the central atom, a great difference of bonding forces with which the outlying groups are bound to the central atom, and affords the possibility of examining related molecules of various degrees of complexity. Preliminary study shows that the temperatures of appreciable decomposition extend over a wide range, from about 220° for lead tetraethyl to about 650" for silicon tetramethyl, and that in at least two cases, germanium tetraethyl and lead tetraethyl, and probably in all of the other cases, the decomposition is predominantly homogeneous and unimolecular. The present paper is an account of the behavior of germanium tetraethyl. Data for the other compounds will be presented in later papers.

The thermal decomposition of gaseous germanium tetraethyl in the range 420–450° is a reaction about 98% homogeneous, and unimolecular down to pressures of about 8 cm. During the course of the decomposition, metallic germanium is deposited as a semi-mirror, or as what amounts to a sputtered film, on the walls of the reaction vessel, and it seems natural to represent the primary reaction as

$$Ge(C_2H_5)_4 \longrightarrow Ge + 4C_2H_5$$

(It must be admitted that this is only a suggested manner of decomposition, and that there is not enough evidence to justify setting up a detailed reaction mechanism. A similar formation of free methyl[2] groups seems to be well established in the decomposition of lead tetramethyl.) The free ethyl groups might then be supposed virtually to unite to form normal bu-

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[1] University Fellow, 1929–1930, The Ohio State University.

[2] Paneth and Hofeditz, *Ber.*, 62, 1335 (1929).

tane, and indeed in a preliminary study of the decomposition of lead tetraethyl (250°), this seems to be essentially what occurs; but in the case of germanium tetraethyl, which decomposes at a temperature almost 200° higher than lead tetraethyl, it is not likely that much actual butane would be formed. Hague and Wheeler[3] noticed slow decomposition of butane at about 435°, and Hurd and Spence[4a] found some decomposition even at 400°. The ethyl groups sloughed off from the germanium may react to give gaseous products very much like the products which Hurd and Spence found for the pyrolysis of n-butane. Our ethyl groups yield 60–70% ethane and ethylene, a proportion which would be obtained if the butane molecules split in the middle, and followed predominantly Equation 2 of Nurd and Spence.[4b] A more detailed account of the decomposition products will be presented in Table V.

Experimental

The course of the decomposition of germanium tetraethyl was followed by measurement of the change of pressure in a reaction vessel. Because of the low vapor pressure of germanium tetraethyl at room temperature, glass membrane manometers of the null type described by Jackson[5] and Gibson[6] were employed. A combination mercury-piston mercury manometer was used for adjusting and measuring the higher air pressures outside the glass membrane, and an ethyl phthalate manometer for measuring the lower pressures (1–2 cm.).

Both pyrex and quartz membranes and reaction chambers (of about 10–15 cc. capacity) were constructed. At 440° even the stiffer pyrex membranes had a slight tendency to soften, although the subsequent change in zero point was not enough to affect the calculations to any great extent. However, to eliminate possible error from this source, clear fused quartz reaction chambers were used in practically all cases. The quartz membrane manometers were made of various degrees of sensitivity, depending on the pressures at which they were intended to serve. A few were estimated to have an extreme sensitivity of about 0.002 mm.

Constant temperature was maintained, within 0.1–0.2°, with a sulfur-bath boiling under the required pressure, generally for convenience at atmospheric pressure. The temperature was measured with a carefully calibrated chromel–alumel thermocouple placed alongside the reaction chamber at its mid-portion.

Samples of germanium tetraethyl were very kindly donated by Professor L. M. Dennis of Cornell University, Professor C. A. Kraus of Brown University, and Mr. Thomas Midgley, Jr.

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[3] Hague and Wheeler, *Fuel Science Practice*, *8*, 560 (1929).

[4] (a) Hurd and Spence, THIS JOURNAL, 51, 3353 (1929); (b) p. 3358.

[5] Jackson, J. *Chem. Soc.*, *99*, 1066 (1911).

[6] Gibson, *Proc. Roy. Soc. Edinburgh*, 33, 1 (1912).

Briefly the procedure in making a run was as follows. A small amount of liquid germanium tetraethyl was sealed up in a small glass bulb with minute capillary ends in such a way that the bulb was filled and only an extremely small quantity of air was left in the capillary ends. This was an important precaution since small amounts of oxygen were found to increase the rate of decomposition quite appreciably. The reaction chamber was connected to a diffusion pump system by a short length of suction tubing, after a bulb of germanium tetraethyl had been placed in the tube a short distance from the chamber. The air pressure was reduced to about 0.001 mm., and during this evacuation the chamber was heated for about fifteen minutes with *a* blast lamp to remove adsorbed gases. The chamber, was then allowed to cool, the bulb rolled down into the chamber and the latter sealed off. The chamber was preheated in an electric furnace to a temperature about 100" below the temperature of appreciable decomposition, and from the pressure of the germanium tetraethyl at this temperature the initial pressure at the temperature of the decomposition run was calculated by means of Charles' law. The reaction chamber was quickly withdrawn from the furnace, thrust into the sulfur bath, clamped fast in a vertical position and a microscope focused on the edge of the membrane manometer pointer when it was in its zero position. Simultaneous readings of pressure and time were taken at one- to two-minute intervals during the first three-quarters of the decomposition, and at longer intervals during the remainder. The data for a typical run at 440.9° are given in Table I.

TABLE I

DATA AND VELOCITY CONSTANT AT 440.9°

Time, minutes	Pressure, cm.	$p_\infty - p$	Velocity constant, k	Time, minutes	Pressure, cm.	$p_\infty - p$	Velocity constant, k
0	30.74	77.16	.....	15.60	68.66	39.24	0.0492
2.45	33.97	73.93	.....	17.25	71.56	36.34	.0465
3.85	37.87	70.03	0.0389	19.12	74.50	33.40	.0432
5.35	42.27	65.63	.0432	26.30	82.80	25.10	....
6.40	45.58	62.32	.0493	29.97	85.62	22.28	.0325
7.75	49.75	58.15	.0512	49.10	94.40	13.50	....
9.44	54.65	53.25	.0521	64.75	97.90	10.00	.0192
10.73	57.98	49.92	.0501	187	106.20	1.70	....
12.65	62.62	45.28	.0509	225	107.10	0.80	....
14.17	65.80	42.10	.0479	267	107.90	.00	....

Column 3 gives the differences between the final pressure and the pressures at the various time intervals. After the first five minutes the velocity constant, k, calculated between successive time intervals by the usual unimolecular equation, assumes a fairly constant value and remains fairly constant until the reaction is about 50% completed, and then falls off considerably.

The fact that the decomposition is almost wholly homogeneous is demonstrated by the data presented in Table II,

TABLE II

HOMOGENEITY OF THE REACTION IN QUARTZ

Run	Temp., °C.	p_{initial} (cm.)	k	k (442°)	Surface ratio
Average	...	..	....	0.0505	1
75	442.3	12.7	0.0550	.0544	10
115	442.2	24 2	.095	.094	40–50
204	441.1	29.5	.095	.099	40–50
206	441.8	35 9	.090	.091	40–50

In Column 5 the velocity constants are corrected to 442°. Since an increase in the surface to volume ratio of 40–50 times does not quite double the velocity constant, it follows that the reaction cannot be more than about 2% heterogeneous. The reproducibility of results from run to run argues for a largely homogeneous reaction. The reaction was also homogeneous in pyrex.

That the decomposition is kinetically unimolecular is shown by the very constant values for the time of half change, $t_{1/2}$, in Col. 6, and by the good

TABLE III

DATA SHOWING UNIMOLECULAR CHARACTER OF THE REACTION

Run	Temp., °C.	Vessel	Pa, cm.	p_∞/p_0	minute.;	k	k (442°)
190	441.6	P	46.5	3.43	16.5	0.048	0.049
198	441.5	P	42.9	3.37	17.0	.052	.054
132	441.7	Q	36.1	3.21	13.5	.056	.057
89	442.3	Q	36.3	3.49	16.5	.048	.047
91	442.4	Q	34.0	3.61	17.0	.050	.049
178	442.0	P	33.0	3.64	12.5	.057	.057
194	440.9	P	30.7	3.51	16 0	.051	.054
85	441.8	Q	30.9	3.56	17.0	.046	.047
43	441.2	P	28.5	3.46	16.5	.051	.053
69	441.6	Q	26.6	3.63	15.0	.054	.055
45	439.9	P	26.2	3.20	16.8	.051	.057
87	441.9	Q	25.4	3.66	15.0	.0475	.048
63	441.3	P	24.6	3.58	17.0	.047	.049
67	441.8	Q	24.6	3.70	17.0	.0495	.050
136	441.4	Q	22.6	3.63	15.0	.051	.0525
83	441.8	Q	21.0	3.61	16.3	.050	.0505
59	442.1	P	19.3	3 20	16.5	.046	.046
65	440.9	Q	18.5	3 90	14.0	.057	.060
41	440.6	P	16.3	3.46	16.5	.0525	.056
134	441.9	Q	15.2	3.76	17.5	.048	.048
71	442.1	Q	13.2	3.80	17.0	.046	.046
79	442.1	Q	13.1	3.54	16.0	.052	.052
39	441.2	P	11.0	3.44	15.0	.052	.054
254	441.2	Q	8.8	3.81	16.5	.053	.055
250	441.0	Q	3.3	4.59	38	.017	.018
252	441.3	Q	1.94	4.89	41	.0135	.0140
248	440.2	Q	1.7	4.98	40	.015	.0164

agreement among the velocity constants of the various runs, indicated in Col. 8 of Table III.

Column 3 indicates the nature of the reaction chamber, pyrex or quartz, Col. 4 the initial pressure, and Col. 5 the ratio of final to initial pressure.

The variation of the velocity constant with temperature is shown in Table IV.

TABLE IV

TEMPERATURE COEFFICIENT DATA

Init. press., cm.	Temp., °C.	Velocity constant, k
Average	442	0.0505
22.7	431	.031
22.2	431.1	.030
26.9	430.6	.031
33.8	419.5	.0153
16.4	419.1	.0142

The velocity constant as a function of temperature may be expressed approximately by the equation

$$\ln k = 32.88 - 51{,}000/RT$$

The energy of activation of this reaction is about 51,000 with a possible error of several thousand calories.

Discussion of Results

Reference to the last three runs of Table III shows that the velocity constant begins to drop off appreciably at low pressures. At a partial pressure of germanium tetraethyl of about 7 cm. the velocity constant is about 0.040. We have estimated the effective diameter of a germanium tetraethyl molecule to be about 7 Å. from the critical density, by using Herzog's[7] empirical equation; and also roughly from the average shadow area[8] of a model of the molecule. From these data we have calculated that z, the total number of collisions per cc. per second, is 6 X 10^{26} and that the number of molecules reacting per cc. per second is **6.3** X 10^{14}. Then from the usual equation

$$k\left(\begin{matrix}\text{molecules}\\ \text{reacting}\end{matrix}/\text{cc./sec.}\right) = 2.5\,ze^{-\left[\frac{E+(\frac{1}{2}n-1)RT}{RT}\right]}\cdot\left[\frac{E+\left(\frac{1}{2}n-1\right)RT}{RT}\right]^{\frac{1}{2}n-1} \qquad \frac{}{2}n-1$$

we obtain a value between 8 and 10, for n the number of so-called active degrees of freedom, or the number of "square terms."

Although the velocity constant falls off at low pressures, the introduction of hydrogen at a pressure of 20 cm. into germanium tetraethyl at a pressure

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[7] **Herzog, *Z. Electrochem.*, 15, 345 (1909).**

[8] **Mack, THIS JOURNAL, 47, 2468** *(1925).*

[9] **Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford,** 1929, **2d ed.,** p. **155.**

of 4.6 cm. failed to raise the value of the constant appreciably. Helium, argon and nitrogen at pressures of about 60 cm. were added to the germanium tetraethyl at about 25 cm. and at first the results seemed to indicate that these inert gases were raising the value of the velocity constant. However, careful analysis of the helium, argon and nitrogen showed the presence of oxygen to the extent of 0.1–0.2%, and since the presence of oxygen in concentrations as large as this in the germanium tetraethyl system increased the velocity constant (in blank determinations) to about the same extent as that found in the case of the inert gases, we concluded that the helium, argon and nitrogen themselves had in reality little, if any, effect on the velocity of the reaction. Our experience with the effect of oxygen in this system leads us to suggest that the increase in the velocity constant observed by Pease[10] and Durgan for the pyrolysis of butane and propane, in the presence of added nitrogen, may be explained by the presence of small quantities of oxygen.

Carbon dioxide, at pressures of 42.4 and 86.5 cm., in germanium tetraethyl at pressures of 21.7 and 8.2 cm., respectively, caused the velocity constant to fall off to 0.034 and 0.024. The lowering was approximately proportional to the partial pressure of the carbon dioxide. This behavior suggests that the activated germanium tetraethyl molecules are being robbed of energy of activation by collision with the carbon dioxide molecules, and indeed the observed falling value of the velocity constant with gradual accumulation of reaction products toward the latter part of the reaction is in line with the same idea.

When hydrogen was introduced into the system with germanium tetraethyl at ordinary pressures (15–25 cm.), the ratios of the final to initial pressures indicated that some of the hydrogen was disappearing in the reaction, and the amounts disappearing were roughly proportional to the pressure of the added hydrogen. Since hydrogen at pressures above about 25 cm. was lost in appreciable amounts by diffusion through quartz membranes of the type we were using, it was necessary to conduct these experiments in pyrex. Analysis of the products of the reaction showed undoubtedly that the disappearance of hydrogen in the reaction was due to the hydrogenation of unsaturated hydrocarbons, as Pease found in the case of ethylene–hydrogen mixtures,[11] although, in the present instance, as suggested below, it seems likely that the hydrogenation reaction occurs at the instant of germanium tetraethyl decomposition.

Analyses of the gaseous products of decomposition were carried out in a modified Bone–Wheeler apparatus. Special reaction vessels were constructed in order to facilitate the handling of the small volumes of gas, amounting to about 10 cc., available for analysis. When the decomposi-

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

[11] Pease, *ibid.*, 52, 1185 (1930).

tion was completed, the chamber was cooled to room temperature and the pressure measured. This pressure, when calculated by Charles' law to the temperature of the decomposition, in nearly all cases checked fairly well with the final pressures actually measured, thus affording evidence that the amounts of high-boiling compounds were very small or zero. The chamber was then cooled to liquid-air temperatures and the vapor phase, consisting of hydrogen and methane, pumped off by means of a Topler pump. The residue was warmed to room temperature, cooled in liquid air and the vapor phase pumped off again. As a rule very small amounts of gas were obtained from this second fractionation. By slow combustion analysis the amounts of hydrogen and methane in the original sample were obtained. The residual gas in the reaction chamber was pumped out and analyzed for saturated and unsaturated hydrocarbons. At first the unsaturation was estimated only as ethylene and higher olefins, according to Hague and Wheeler. In later analyses the higher olefins were separated into groups according to Hurd and Spence. Combustion of the saturated hydrocarbons gave the average carbon content per molecule, and showed the presence of practically nothing except ethane and propane. No great accuracy is claimed for the analysis, but on any given sample it is probably correct to within a few per cent. Typical analyses are given in Table V. It will be noted from the table that the total percentage of unsaturation is practically independent of the two methods, (a) and (b), employed, although the separation of the different groups of the unsaturated fraction according to the Hurd and Spence method (b), is undoubtedly more reliable.

TABLE V

ANALYSIS OF GASEOUS PRODUCTS

					Added hydrogen		
Run	168[a]	178[a]	194[b]	198[b]	170[a]	174[a]	182[a]
Hydrogen, %	11.6	10.6	10.6	11.5	11.0	11.0	11.0
Methane, %	12.2	9.9	7.5	9.5	14.8	15.5	15 0
Ethane, %	29.9	34.2	41.5	43.9	51.4	45.0	563
Propane, %	10.3	8.6	3.3	2.9	4.0	5.4	0.0
Ethylene, %	29.2	29.6	21.7	17.3	14.8	16.7	14.3
Propylene + butylene, %	.	. .	12.7	12.9	. . .		. .
Isobutylene, etc., %			1.6	1.7	. .		
Acetylenes, %	. . .	.	1.4	0.3	.		0.3
Higher olefins (propylene, etc.), %	6.9	9.8			3.8	6.1	2.8

[a] Hague and Wheeler method of analysis of unsaturation. [b] Hurd and Spence method.

Among the experiments in which hydrogen was added to the reaction system were three, namely, Runs 170, 174, 182, with the added hydrogen at a pressure of about 50 cm., which are tabulated above. In order to obtain a comparison between the composition of the product gases in these cases and the normal decompositions in the absence of added hydrogen, it was assumed as an approximation that about 11% of hydrogen would be formed in all of the decompositions, and the added hydrogen was not included in the listed percentage composition.

The data show clearly that in the presence of added hydrogen the decomposition yields a higher proportion of saturated hydrocarbons. Still, a large part of the unsaturation always remains. In addition, the times of half change, $t_{1/2}$, had about the same value as in the absence of added hydrogen. This indicates that the hydrogenation takes place simultaneously with the decomposition of the germanium tetraethyl molecule, and not in a later independent reaction, It seems probable that during the instant immediately following decomposition, while an unsaturated molecule (C_2H_5, C_2H_4, etc.), still has its share of the energy of activation from the decomposition, it is much more easily hydrogenated by collision with hydrogen than after the loss of this energy by collision with other molecules.

When the decomposition was carried out in the presence of *added* ethylene, part of the ethylene was found to disappear during the reaction. Probably there were two factors involved, hydrogenation and polymerization to the more stable butylene, as Pease found in the case of ethylene–hydrogen mixtures at this temperature. This polymerization, with large amounts of added ethylene, had the effect of raising the velocity constant during the first part, and of lowering it during the last part, of the reaction. This effect is to be expected since the calculation of the velocity constant involves the final pressure and since the polymerization lowers the ratio of final to initial pressure markedly. The polymerization of ethylene comes practically to a stop toward the later stages of a run, not only because of the decreasing partial pressure of the ethylene, but probably also because of the decreasing effect of the falling concentration of germanium tetraethyl on the polymerization. Taylor[12] and Jones have recently claimed that decomposition of metal alkyls induces ethylene polymerization.

In a *normal* run, in the absence of *added ethylene,* it seems that the velocity constant and the time of half change of the primary decompositions of germanium tetraethyl are unaffected by any reactions occurring among the product gases, if such reactions occur at all, or at least that these latter consecutive reactions must be rapid compared with the slower primary decomposition. Other considerations, as well, seem to justify the validity of using pressure measurements as a means of following the course of the primary decomposition.

The above analyses also show that the products vary slightly in proportion from run to run. This is also indicated by the variation in the values of the ratios of final to initial pressure in Table III. It is to be noted, though, that the absolute variations in the ratios of final to initial pressures

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[12] **Taylor** and Jones, Tars JOURNAL, 52,1111 (1930).

are not to be taken too seriously, since there is one important source of error in the determination of these values. The final pressure was measured in the sulfur-bath; the initial pressure in an electric furnace. It was not always expedient to see that the chamber took exactly a vertical position in both cases. Hence the weight of the manometer pointer would cause error in each measurement which would be magnified in the ratio. Since the velocity constants were calculated from differences in pressure in the sulfur-bath, they are reliable in spite of the possible error in the absolute pressures.

Summary

The thermal decomposition of gaseous germanium tetraethyl in the temperature range 420–450° has been studied and has been found to be about 98% homogeneous, and unimolecular down to a pressure of about 8 cm.

At about 7 cm. the value of the velocity constant begins to fall off, but the addition of hydrogen gas to the reaction system does not raise the constant appreciably.

The energy of activation is about 51,000, with a possbile error of several thousand calories, and the velocity constant is given by the equation, $\ln k = 32.88 - 51{,}000/RT$. The number of active degrees of freedom calculated at the pressure where the velocity constant begins to fall off is between 8 and 10.

The reaction yields metallic germanium, and analysis of the gases from the decomposition shows essentially the products obtained by pyrolysis of butane. Added hydrogen and ethylene enter into hydrogenation and polymerization reactions in the gaseous system. Added carbon dioxide cuts down the velocity constant, but nitrogen, helium and argon have little, if any, effect.

It seems justifiable to measure the course of this decomposition by pressure changes, and the pressures have been measured with quartz and pyrex membrane manometers.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THERMAL DATA ON ORGANIC COMPOUNDS. IX. A STUDY OF THE EFFECT OF UNSATURATION ON THE HEAT CAPACITIES, ENTROPIES AND FREE ENERGIES OF SOME HYDROCARBONS AND OTHER COMPOUNDS[1]

BY GEORGE S PARKS[2] AND HUGH M. HUFFMAN[3]

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In the three papers[4] of this series immediately preceding the present one, we presented data for the heat capacities, entropies and free energies of more than thirty hydrocarbons. These results were utilized in determining the effect (1) of increasing the length of the chain in an aliphatic hydrocarbon, (2) of inserting side branches on the main chain and (3) of introducing one or more phenyl groups. The present investigation is essentially similar in character to those which have gone before it but deals particularly with the problem of unsaturation, *i. e.*, the effect of the C=C bond on the heat capacities, entropies and free energies of hydrocarbons and other compounds. In this study we have used many of the data previously obtained and also have made new heat capacity measurements on the following twelve compounds fumaric acid, maleic acid, succinic acid, pentene-2, trimethylethylene, n-pentane, cyclohexene, methylcyclohexane, di-isobutylene, stilbene, dibenzoylethylene and dibenzoylethane.

Materials

Fumaric Acid, Maleic Acid, Succinic Acid, Dibenzoylethylene and Dibenzoylethane.—These substances were supplied to us in pure form by Professor James B. Conant of Harvard University. Concerning them he writes as follows.

"The fumaric acid was a commercial material (presumably prepared by the catalytic oxidation of benzene) which I recrystallized three or four times from water. The succinic acid was a high-grade commercial product which I personally recrystallized twice.

"The maleic acid was prepared by redistilling in glass maleic anhydride. This anhydride was then dissolved in distilled water and crystallized by concentration in *vacuo*. This is the only method which gives a really pure maleic acid free from fumaric. The melting point given in the literature is 130–131°. If slowly heated in the ordinary melting point apparatus. the acid I am sending you melts at this temperature. It shows a somewhat higher melting point if rapidly heated. Personally I am inclined to

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[1] This paper contains results obtained in an investigation of the heat capacities and free energies of some typical hydrocarbon compounds, listed as Project No. 29 of the 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. 29.

[3] American Petroleum Institute Research Associate.

[4] Parks, Huffman and Thomas, THIS JOURNAL, 52,1032 (1930); Huffman, Parks and Daniels, *ibid.*, 52, 1547 (1930); Huffman, Parks and Thomas, *ibid.*, 52,3241 (1930).

think that this higher value may be nearer the truth, in spite of the statements in the literature.

"The dibenzoylethane ($C_6H_5CO(CH_2)_2COC_6H_5$) and ethylene (*trans*-$C_6H_5COCH{=}CHCOC_6H_5$) were prepared according to the methods described by Lutz and myself.[6] They were purified by repeated recrystallization from alcohol. In this connection it should be noted that the ethane sample was very kindly donated by Professor Lutz of the University of Virginia."

Pentene-2, Trimethylethylene, *n*-Pentane and **Di-isobutylene.**—These four hydrocarbons were very carefully prepared for us by Dr. H. E. Buc of the Standard Oil Development Company. Their preparation is difficult, and none of them could be obtained in the open market in a state of purity sufficient for our work.

The pentene-2, $CH_3CH{=}CHC_2H_5$, was prepared by dehydration of secondary amyl alcohol. The product was dried with alkali and then refractionated over anhydrous copper sulfate. Two additional fractionations in a special still gave a final product which boiled between 36.27 and 36.31" at 765 mm. In spite of the very small boiling range of this material, we were never able to crystallize it completely in the course of our specific heat measurements. The explanation of this fact is probably to be found in geometrical isomerism, since pentene-2 may exist in cis and trans forms similar to maleic and fumaric acids. Undoubtedly one of these forms of pentene-2, probably the trans, is somewhat more stable thermodynamically than the other; but it is quite possible that some of each was produced in the present synthesis and was carried through the fractional distillations into the final product. In this event we were really working upon a solution rather than on a pure compound. However, the specific heats of the two forms should not differ greatly, and therefore we believe that our data for this substance in the liquid state are fairly reliable. The incomplete crystallization prevented us from obtaining accurate values for the crystals or for the heat of fusion.

The trimethylethylene, $(CH_3)_2C{=}CHCH_3$, was prepared from a cruder sample of this material by fractional distillation. Fifteen successive fractionations, starting with about 1800 cc. and ending with 200 cc., gave a final product which boiled at 38.5–38.6°, 765 mm. This material crystallized in satisfactory fashion and was evidently fairly pure. It is interesting to note that the compound does not admit of geometrical isomerism.

The *n*-pentane was similarly prepared from a sample of crude "normal pentane" (a petroleum product) by an elaborate series of fractional distillations It boiled at 35.75–35.80" (746 mm.) and, when cooled by liquid air, produced crystals which exhibited a very sharp melting point at 143.4°K. Without doubt this was one of the purest hydrocarbon samples that we have ever studied.

The di-isobutylene was prepared by polymerization of isobutylene and subsequent fractionation. It presumably has the formula $(CH_3)_3CCH{=}C(CH_3)_2$. On being cooled with liquid air, it first formed a glass, which crystallized completely as it warmed up. While the melting point of the crystals was not sharp, we believe that our thermal data for this substance are fairly reliable, although probably not of the same order of accuracy as for the other compounds.

Cyclohexene and **Methylcyclohexane.**—High grade Eastman products were subjected to a series of fractional distillations and to successive dryings with anhydrous copper sulfate. The final sample of cyclohexene boiled at 83.0°, 765 mm.; that of the methylcyclohexane boiled at 100.95–101.00°, 763 mm. Both substances exhibited sharp melting points after crystallization with liquid air. .

Stilbene.—Eastman's stilbene (m. p. 120°) was subjected to four crystallizations from ethyl alcohol. The final product melted at 124.2°. It is considered to be the trans form.

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[5] Conant and Lutz, THIS JOURNAL, 45,1303 (1923).

Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. The apparatus and details of experimental procedure have been fully described in other places.[6] In view of the accuracy of the various measurements involved, the error in the experimental values thereby obtained is probably less than 1%, except in so far as impurities in a hydrocarbon sample, such as that of di-isobutylene, may cause premelting or otherwise influence the results.

The specific heats and the fusion data, expressed in terms of the 15° calorie[7] and with all weights reduced to a vacuum basis, appear in Tables I and II.

TABLE I

SPECIFIC HEATS

FUMARIC ACID: Crystals

Temp., °K.	91.3	97.2	104.7	112.5	135.0	144.1	155.6	175.2
C_p **per** g.	0 128	0.135	0 141	0.148	0.168	0.174	0.183	0.199
Temp., °K.	184.9	193 5	215 2	234 6	255 7	275.6	288.0	297.1
C_p **per** g.	0.206	0.212	0.231	0.246	0.261	0 275	0.285	0.292

MALEIC ACID: Crystals

Temp., °K.	91.0	97.5	103.4	124.0	136.4	149.7	163.5	177.7
C_p **per** g.	0.124	0.130	0.134	0.150	0.160	0.170	0.180	0.190
Temp.. °K.	189.0	199.6	220.7	247.1	275.1	281.5	287.9	294.4
C_p **per** g.	0.198	0.207	0.222	0.241	0.262	0,268	0.273	0.279

SUCCINIC ACID: Crystals

Temp., °K.	93.4	100.9	113.7	125.5	139.7	154.7	185.1	215.0
C_p **per** g.	0.134	0.141	0.152	0.162	0.174	0.187	0.211	0.237
Temp., °K.	244.3	260.0	265.9	272.4	274.6	276.0	283.4	289.8
C_p **per** g.	0.262	0.277	0.289	0.344	0.295	0.289	0.296	0.303

PENTENE-2: Liquid

Temp., °K.	136.1	152.8	169.0	201.2	230.8	260.6	275.1	289.1
C_p **per** g.	0.436	0.439	0.443	0.458	0.474	0.492	0.504	0.515

TRIMETHYLETHYLENE: Crystals

Temp., °K.	92.7	93.9	97.3	101.0	104.8	107.5	111.3
C_p **per** g.	0.238	0.240	0.247	0.254	0.261	0.266	0.277

Liquid

Temp.. °K.	143.9	152.8	173.4	183.8	201.4	203.4	213.7	231.5
C_p **per g.**	0.448	0.448	0.449	0.452	0.459	0.461	0.466	0.471
Temp., °K.	233.5	253.5	263.4	275.4	283.4	289.0	293.9	
C_p **per g.**	0.473	0.485	0.491	0.498	0.505	0.508	0.512	

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[6] Parks, THIS JOURNAL, **47,** 338 (1925); also Parks and Kelley, *J. Phys. Chem.,* **30,** 47 (1926).

[7] The factor 0.2390 has been used in converting from the joule to the 15° calorie.

TABLE I (Continued)

n-PENTANE: Crystals

Temp., °K	92.8	97.9	102.7	108.6	114.8	121.0	126.7	132.2
C_p per g	0.233	0.243	0.251	0.261	0.271	0.282	0.292	0.306

Liquid

Temp., °K	149.9	154.1	162.4	169.9	185.5	200.4	214.9
C_p per g	0.465	0.465	0.468	0.468	0.473	0.479	0.485
Temp., °K	231.2	244.5	260.2	274.8	279.2	284.7	290.0
C_p per g	0.494	0.501	0.514	0.528	0.531	0.536	0.540

CYCLOHEXENE: Crystals I

Temp., °K	92.0	99.2	105.7	112.6	119.3	125.7	131.8
C_p per g	0.155	0.164	0.171	0.178	0.185	0.192	0.199

Crystals II

Temp., °K	146.5	151.2	157.1	162.8
C_p per g	0.280	0.286	0.294	0.312

Liquid

Temp., °K	175.2	177.1	185.4	197.1	211.9	227.0
C_p per g	0.336	0.337	0.342	0.349	0.358	0.368
Temp., °K	243.8	256.7	275.8	280.6	286.9	293.2
C_p per g	0.382	0.390	0.407	0.411	0.419	0.423

METHYLCYCLOHEXANE: Crystals

Temp., °K	93.2	99.2	105.5	111.6	112.2	118.2	124.5	130.0
C_p per g	0.154	0.162	0.170	0.178	0.179	0.186	0.195	0.205

Liquid

Temp., °K	151.4	157.1	170.3	182.6	199.4	214.3
C_p per g	0.339	0.343	0.351	0.359	0.368	0.378
Temp., °K	229.4	244.9	260.0	275.4	285.2	294.2
C_p per g	0.389	0.400	0.412	0.426	0.436	0.443

DI-ISOBUTYLENE: Crystals

Temp., °K	92.1	94.5	97.0	103.3	110.0	124.2	125.5	131.3
C_p per g	0.188	0.195	0.202	0.217	0.226	0.247	0.249	0.260

Liquid

Temp., °K	183.0	189.1	210.5	230.1	251.8	275.2	281.2	296.0
C_p per g	0.407	0.410	0.425	0.439	0.454	0.475	0.481	0.497

STILBENE:[a] Crystals

Temp., °K	92.3	93.9	101.7	109.8	124.3	134.0	148.3	164.9
C_p per g	0.116	0.118	0.123	0.129	0.140	0.148	0.159	0.174
Temp., °K	179.6	198.8	211.7	227.6	254.4	264.8	276.4	292.8
C_p per g	0.188	0.206	0.219	0.235	0.262	0.273	0.284	0.301

DIBENZOYLETHYLENE: Crystals

Temp., °K	88.8	97.5	107.8	127.0	138.6	151.5	165.0	178.5
C_p per g	0.111	0.117	0.126	0.141	0.150	0.161	0.172	0.183
Temp., °K	192.5	206.3	230.3	251.8	258.5	277.6	284.0	291.9
C_p per g	0.196	0.208	0.231	0.251	0.257	0.277	0.284	0.290

TABLE I (*Concluded*)

DIBENZOYLETHANE: Crystals

Temp., °K.	93.2	99.8	107.8	117.1	124.0	134.1	145.8	156.0
C_p per g.	0.115	0.121	0.128	0.135	0.141	0.151	0.161	0.171
Temp., °K.	164.6	169.5	172.7	180.3	182.4	186.2	190.6	194.4
C_p per g.	0.179	0.183	0.188	0.203	0.207	0.219	0.200	0.200
Temp., °K.	214.0	243.8	255.4	276.0	276.3	281.9	289.0	296.0
C_p per g.	0.215	0.241	0 252	0.272	0.272	0.277	0.284	0.292

[a] In this connection we wish to acknowledge our indebtedness to Mr. A. C. Daniels of this Laboratory, who very kindly made the measurements on stilbene for us.

TABLE II

FUSION DATA[a]

Substance	M. p., °K.	Heat of fusion (cal. per g.) 1st result	2d result	Mean
Trimethylethylene	138.9	25.82	25.66	25.74
n-Pentane	143.4	27.75	27.75	27.75
Cyclohexene	169 0	9.56	9.58	9.57
Methylcyclohexane	146.2	16.25	16.24	16.24
Di-isobutylene	172	16.83	...	16.83

[a] In the calculation of these fusion values, the marked rise in the specific heat of the crystals as the melting point is approached was attributed to premelting; and the heat absorbed in this region in excess of that obtained by extrapolation of the specific heat data at lower temperatures was added to the heat absorbed at the melting point.

TABLE III

TRANSITION DATA

Substance	Transition temperature, °K.	Heat of transition (cal. per g.) 1st result	2nd result	Mean
Cyclohexene	138.7	12.19	11.53	11.86

For comparison with these values the literature[8] contains only very meager data. Our extrapolated specific heat curve for succinic acid is about 6% above the value obtained by Hess at a mean temperature of 25° and 3.5% above that of deHeen at 35°. For n-pentane Schlesinger has made determinations on the liquid at −78 and 0°. His results are below our curve by 0.2 and 2.3%, respectively. The specific heat value of Nadejdin for "isoamylene," presumably trimethylethylene, at *a* mean temperature of −3.5° is only 0.4% above our curve for this substance.

Cyclohexene was found to exist in two crystalline forms with a fairly definite transition temperature at 138.7°K., and the heat of transition was measured by the same procedure used in the fusion determinations. The data thus obtained are recorded in Table III. In this connection it is noteworthy that the heat of transition is about 25% greater than the heat of fusion.

In the cases of succinic acid and dibenzoylethane the specific heat curve for the crystals show a small maximum or "hump." Such a phenomenon

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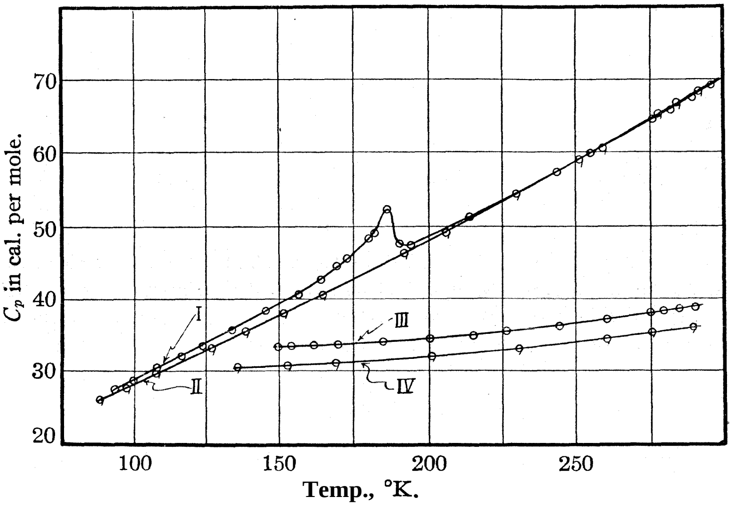
[8] Landolt–Börnstein–Roth–Scheel, "Tabellen," Julius Springer. Berlin. 1923, pp. 1267 and 1271.

has been observed for several other compounds which have been studied in this Laboratory and is undoubtedly real, although its explanation is not apparent. For dibenzoylethane the hump comes at about 187°K. (see Fig. 1) and the heat effect in excess of the normal specific heat amounts to **0.22** cal. per g. or **52** cal. per mole. The two parts of the heat capacity curve below and above this transition region fit together quite smoothly, indicating that the same crystalline form probably exists over the entire temperature range. A similar hump was found for succinic acid at about 272°K. with a heat effect of 41 cal. per mole.



Pig. 1.—Curve I refers to dibenzoylethane; II to dibenzoylethylene; III to n-pentane; IV to pentene-2.

A careful study of the thermal data indicates that the withdrawal of a mole of hydrogen, with the resulting production of an ethylenic double bond in the parent compound, ordinarily lowers somewhat the molal heat capacity at a given temperature. Outside of the hump region the effect is hardly noticeable in the case of crystalline dibenzoylethane and dibenzoylethylene, where the change in the molecular weight is less than 1%, while it is quite appreciable with liquid n-pentane and pentene-2, where the change in molecular weight is about **3%.** These examples are, perhaps, rather extreme cases, and, accordingly, we have represented them graphically in Fig. 1.

The lowering in molal heat capacity on formation of an olefin is undoubtedly due to the decreased vibrations (as a result of the increased constraints) of the carbon atoms adjacent to the double bond rather than to a loss of the thermal energy associated with the vibrations of the two hydrogen atoms. This last is probably negligible at all temperatures up to that of the room.

Discussion

Entropies **of the** Compounds.—Using the data contained in Tables I, II and III in conjunction with the third law of thermodynamics, we have calculated the molal entropies at 298.1°K. for all the compounds except pentene-2. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffman[9] for estimating the entropy increase for the crystals, Col. 2 of Table IV, from 0 to 90°K. The various entropy increments from 90 to 298.1°K., which appear in Cols. 3, 4 and 5 of the table, were obtained by the usual methods directly from the experimental data. The results for the total entropy in calories per degree appear under the heading S_{298} in the last column. In the case of stilbene, which is normally crystalline, we have roughly calculated the entropy of fusion[10] at 298° so as to obtain a value for its entropy as a liquid, even though the liquid state is unstable at this temperature.

TABLE IV

ENTROPIES OF THE SUBSTANCES PER MOLE

Substance	Crystals 0–90°K.	Crystals Above 90°K.	Fusion	Liquid	S_{298}
Fumaric acid	12.31	27 34	...	...	39.7
Maleic acid	12.10	25.97		...	38.1
Succinic acid	13.17	28.86[a]	...	. .	42.0
Trimethylethylene	13.12	8.37	12.99	25.00	59.5
n-Pentane	13.53	9.09	13.95	25.42	62.0
Cyclohexene	11 76	18.13[b]	4.65	17.28	51.8
Methylcyclohexane	13.08	8.77	10.90	26.59	59.3
Di-isobutylene	15.24	18 03	10.96	27.12	71.4
Stilbene (solid)	19.81	40.16	...	...	60.0
Stilbene (liquid)	...	...	15.7	...	75.7
Dibenzoylethylene	24.88	51.42	...	...	76.3
Dibenzoylethane	24 79	52.81"	...	...	77.6

[a] This value includes 0.15 E. U. for the entropy of the hump at 272°K.

[b] This value includes the entropy increase for both crystalline forms as well as the entropy effect (7.11 E. U.) for the transition between them.

[c] This value includes 0.28 E. U. for the entropy of a hump at 187°K.

We now possess entropy values for a number of unsaturated compounds and are in a position to compare these with the entropies of the corresponding saturated substances. We have made such a comparison in Table V.

In eight cases out of the nine cited the entropy of the unsaturated compound is appreciably less than that of the corresponding saturated one.

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[9] Kelley, Parks and Huffman, J. *Phys. Chem.*, 33,1802 (1929).

[10] This approximate calculation of the entropy of fusion was made by the equation $\Delta S_{298} = (\Delta H \text{ fusion})/T_{\mathrm{M}} - AC, \ln (T_{\mathrm{M}}/298)$, where A H and T_{M} are, respectively, the molal heat of fusion and the melting point. In this case ΔC_p, the difference between the molal heat capacity of the liquid and crystals, was assumed to be approximately 9 cal. For AH, we have used 7200 cal. per mole ("International Critical Tables," Vol. V, p. 134).

TABLE V

A COMPARISON OF THE ENTROPIES OF SOME SATURATED AND UNSATURATED ORGANIC COMPOUNDS

Entropy of the saturated compound		Entropy of the unsaturated compound		Entropy decrease with unsaturation, E. U.
Succinic acid	42.0	Fumaric acid	39.7	2.3
Succinic acid	42.0	Maleic acid	38.1	3.9
Dibenzoylethane	77.6	Dibenzoylethylene	76.3	1.3
2-Methylbutane	60.8	Trimethylethylene	59.5	1.3
2,2,4-Trimethylpentane	75.2	Di-isobutylene	71.4	3.8
Dibenzyl	64.6	Stilbene	60.0	4.6
Cyclohexane	49.2	Cyclohexene	51.8	−2.6
Cyclohexane	49.2	Benzene	41.9	2.4 X 3
Methylcyclohexane	59.3	Toluene	52.4	2.3 X 3

In these eight comparisons the differences, while by no means constant, average 2.7 E. U. per double bond, or mole of hydrogen withdrawn. In the cyclohexane–cyclohexene comparison, however, the entropy of the latter is actually greater by 2.6 E. U. In our opinion this anomaly is to be attributed to an abnormally low entropy value for cyclohexane, which (like benzene) possesses great molecular symmetry and is somewhat unique in character.

In a preceding paper[11] it was shown that the entropy of a liquid paraffin or benzenoid hydrocarbon could be calculated quite accurately by the empirical equation, $S_{298} = 25.0 + 7.7n - 4.5r + 19.5p$. Here n and p represent, respectively, the number of aliphatic carbon atoms and phenyl groups in the molecule, and r ordinarily refers to the number of methyl branches attached on the main aliphatic chain. In order to apply the equation to olefin hydrocarbons we might now add the term $-2.7e$, where e represents the number of ethylenic double bonds within the acyclic portion of the compound. The equation for liquid olefins then becomes, $S_{298} = 25.0 + 7.7n - 4.5r - 2.7e + 19.5p$. Using it, we calculate the following entropies: trimethylethylene, 56.3 E. U.; di-isobutylene, 70.4 E. U.; and stilbene, 76.7 E. U. These values differ from the experimental results of Table IV by -3.2, -1.0 and $+1.0$ E. U., respectively. Thus the above formula, though not precise, may be useful in roughly estimating the entropies of olefin hydrocarbons.

The Free Energies of the Compounds

We have also calculated the free energies of these eleven compounds by means of the third law of thermodynamics and the fundamental thermodynamic equation, $AF = AH - TAS$.

The essential data are given in Table VI. For obtaining the AH of formation for succinic acid we have used the heat of combustion reported by Verkade, Hartman and Coops,[12] and for dibenzoylethylene and dibenzoyl-

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[11] Huffman, Parks and Daniels, THIS JOURNAL, 52, 1553 (1930).

[12] Verkade, Hartman and Coops, *Rec. trav. chim.*, 47,608 (1928).

ethane we have employed some unpublished values, recently obtained in our Laboratory by Mr. T. R. Lumb. In the cases of the remaining eight compounds we have taken the heats of combustion as given in the "International Critical Tables."[13] For our present purpose we have converted all these combustion data to 298.1°K. The ΔH_{298} values were then calculated by use of 68,330 and 94,270 cal.[4] for the heats of combustion 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 and hydrogen were taken as **1.3** and 14.8 E. U.[4] per gram atom.

TABLE VI

THERMAL DATA AT 298.1°K.

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

Substance	Heat of combustion at constant pressure	ΔH_{298} Cal.	ΔS_{298} E U.	ΔF°_{298} Cal.
Fumaric acid (S)	319.900	−193,800	−122.7	−157,200
Maleic acid (S)	326.000	−187,700	−124.3	−160,600
Succinic acid (S)	356,900	−225,100	−150.0	−180,400
Trimethylethylene	795,700	− 17,300	− 95.0	+ 11,000
n-Pentane	833,100	− 48,300	−122.1	− 11,900
Cyclohexene	891,700	− 15,600	−104.0	+ 15,400
Methylcyclohexane	1,091,400	− 46,800	−157.0	0,000
Di-isobutylene	1,252,000	− 48,800	−175.8	+ 3,600
Stilbene (S)	1,764,600	+ 34,800	−135.8	+ 75,300
Dibenzoylethylene (S)	1,885,300	− 33,000	−171.1	+ 18,000
Dibenzoylethane (S)	1,920,700	− 65,900	−199.4	− 6,500

The molal free energies appear in the last column of the table. For comparative purposes the accuracy of these values is largely limited by the accuracy of the combustion data employed. In the cases of di-isobutylene and stilbene the present combustion values may be in error by as much as five thousand calories; and therefore the free energies are uncertain to this extent. On the other hand, in the cases of the three dibasic acids the combustion results are accurate to about three hundred calories. For the remaining compounds the values are probably reliable to one or two thousand calories.

The results for maleic and fumaric acids provide quantitative thermodynamic evidence on the interesting problem of geometrical isomerism. It is well known that the cis form, maleic acid, tends to change over into the *trans* isomer. fumaric acid, and the present data show that for the transformation $\Delta F_{298} = -6600$ cal. Hence, the reaction should ***go*** virtually to completion. Furthermore, such a marked difference in the values for two geometrical isomers serves to emphasize the specific influence of structure in determining the free energies of unsaturated compounds.

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[13] **"International Critical Tables," Vol. V, p.** 163.

To develop further this last thesis, we have calculated from the data of this and the immediately preceding papers the free energy changes accompanying a number of reactions in which a saturated compound loses hydrogen and yields an olefinic or benzenoid compound. The results appear in Table VII. For completeness we have also included a value for the conversion of ethane into ethylene derived by Pease and Durgan.[14] It is evident that ΔF_{298} for the process of forming an olefin varies greatly, and no generalization concerning this quantity can be made with any certainty. However, the respective values for the production of ethylene, trimethylethylene and di-isobutylene indicate that ΔF for the dehydrogenation process probably decreases rapidly as we proceed up the series of olefin hydrocarbons.

In the two parallel cases involving the production of benzene and toluene from cyclohexane and methylcyclohexane, respectively, it is noteworthy that the ΔF values are practically identical, *i. e.*, about 24,000 cal. for the loss of three moles of hydrogen. Here the average ΔF_{298} per mole of hydrogen withdrawn (8000 cal.) is considerably less than in the case of any olefin compound except di-isobutylene.

TABLE VII

FREE ENERGY CHANGES ACCOMPANYING SOME DEHYDROGENATION REACTIONS

Saturated compound		Unsaturated compound	ΔF°_{298}, cal.
Succinic acid	=	H_2 + Maleic acid	+29,800
Succinic acid	=	H_2 + Fumaric acid	23,200
Dibenzoylethane	=	H_2 + Dibenzoylethylene	24,500
Ethane	=	H_2 + Ethylene	22,600
2-Methylbutane	=	H_2 + Trimethylethylene	17,600
2,2,4-Trimethylpentane	=	H_2 + Di-isobutylene	9,200
Dibenzyl	=	H_2 + Stilbene	15,200
Cyclohexane	=	H_2 + Cyclohexene	11,700
Cyclohexane	=	$3H_2$ + Benzene	8,000 X 3
Methylcyclohexane	=	$3H_2$ + Toluene	8,000 X 3

Before concluding, the authors wish to thank the Research Laboratory of the Standard Oil Development Company and Professor James B. Conant of Harvard University for the valuable compounds which made this research possible.

Summary

1. The specific heats of twelve organic compounds, including seven hydrocarbons, have been measured over a wide range of temperatures. The heats of fusion of five of the hydrocarbons and the heat of transition of cyclohexene have also been determined.

2. The entropies of eleven of the compounds have been calculated from these heat capacity data. In general the entropy of an unsaturated sub-

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[14] Pease and Durgan, THIS JOURNAL, 50, 2715 (1928).

stance was found to be slightly less than that of the corresponding saturated compound.

3. The corresponding free energies have also been calculated. The free energy change in dehydrogenation reactions was found to vary greatly, and it is apparent that the effect of unsaturation in determining the free energy value of an organic compound is very specific.

STANFORD UNIVERSITY, CALIFORNIA

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

THE ALCOHOLYSIS OF CERTAIN 1,3-DIKETONES AND BETA-KETONIC ESTERS

BY WALTER M. KUTZ AND HOMER ADKINS

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This investigation was undertaken originally for the purpose of studying the influence of structure on the extent of formation and cleavage of carbon to carbon linkages in organic compounds. The ideal condition for a study of this nature would be a perfectly reversible reaction in which the concentration of various sets of reactants at the equilibrium point could be measured accurately. The quantitative work which has been done previously in connection with this problem has been concerned chiefly with the extent of dissociation of hexa-substituted ethanes. The interpretation of the experimental data in terms of the relation of structure to the strength of the carbon to carbon linkage between the substituted methyl groups is complicated by the fact that the dissociated radical is apparently in equilibrium with compounds having a quinoid structure. In addition to the rather large volume of literature upon the hexa-substituted ethanes there has been, also, a paper by Miss Edith Usherwood[1] upon the position of the equilibrium point in the aldolization of isobutyric aldehyde.

The Claisen or acetoacetic ester condensation since the publication of Dieckmann's work[2] has been considered to be a reversible reaction, and it seemed upon preliminary consideration to be better suited than any other reaction for an investigation of the relationship of the structure of a compound to the strength of carbon to carbon linkages. In general terms the Claisen synthesis may be considered to involve the elimination of a molecule of alcohol through the reaction of the alkoxy group of an ester with a hydrogen on a carbon atom alpha to a carbonyl or other activating group in the presence of such reagents as sodium, sodium ethoxide or sodamide. The type reaction may be represented as

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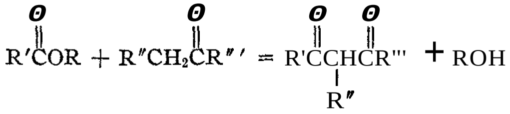
[1] **Usherwood,** *J. Chem. Soc.*, 123, 1917 (1923).

[2] Dieckmann, *Ber.*, **33,** 2670 (1900).



$$R'\overset{O}{\overset{\|}{C}}OR + R''CH_2\overset{O}{\overset{\|}{C}}R''' = R'\overset{O}{\overset{\|}{C}}\underset{R''}{\underset{|}{CH}}\overset{O}{\overset{\|}{C}}R''' + ROH$$

It is obvious that this simple formulation is very far from giving an adequate picture of this reaction. Sodium ethoxide for example forms addition compounds with the ester and the ketones. The ketones also compete through their enol forms for the metal of the alkoxide. However, these complications do not make it impossible profitably to utilize this action for the study of the relation of structure to the extent of the cleavage of the carbon linkage, although they may make very difficult an interpretation of the results. An attempt was therefore made to determine the concentration at equilibrium of the reactants in the synthesis and alcoholysis of acetoacetic ester.

Higley[3] found that he could obtain acetoacetic ester in a 36% yield (based on the sodium ethoxide) through the reaction of **0.4** mole of ethyl acetate and **0.14** mole of sodium ethoxide. He believed that this represented the concentration of acetoacetic ester at equilibrium. McElvain[4] showed that a **68%** yield of the keto ester (based on the sodium ethoxide) could be obtained if the alcohol formed in the condensation were distilled out of the reaction mixture before the ester was isolated. He used 6 moles of ethyl acetate and *0.5* mole of sodium ethoxide. The reaction mixture was not homogeneous after the removal of the alcohol, so that both of these factors tended to drive the condensation toward completion. McElvain's results have been duplicated and the extent of condensation of ethyl acetate in a homogeneous reaction mixture determined both by synthesis and alcoholysis to be from **44** to 50% in so far as this may be judged through the isolation of acetoacetic ester. This last statement is based upon the results of the following experiments in which the homogeneity of the reaction mixture was maintained through the use of a large excess of ethyl acetate.

1. One-half mole of sodium ethoxide and 6 moles of ethyl acetate were refluxed for periods of from ten to ninety-six hours. The reaction mixture was then acidified with 35 ml. of acetic acid in 70 ml. of water and the aqueous layer extracted twice with 50-ml. quantities of ether after the removal of the layer of acetoacetic ester. The fractionation of the products gave from 32 to 33 g. of ester boiling at 84–87° (25 mm.). This represents a yield of 50 to 51%.

2. One-half mole each of acetoacetic ester, of sodium ethoxide and of ethanol were refluxed for twenty-four hours in six moles of ethyl acetate. The reaction mixture was worked up as described above and from 29 to 30 g. of acetoacetic ester obtained.

3. One-half mole of sodium ethoxide and six moles of ethyl acetate were allowed to react and the alcohol and excess simple ester distilled off as described by McElvain. One mole of ethanol and six moles of ethyl acetate were then added to the solid reaction products and the whole refluxed for twenty-four or forty-eight hours. Upon working up

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[3] Higley, *Am.* Chem. J., 37, 299 (1907).

[4] McElvain, THIS JOURNAL, 51, 3124 (1929).

the reaction mixture 28.5 to 29 g. of acetoacetic ester was obtained. This is to be contrasted with the yields of from 43 to 44 g. of keto ester obtained if it were isolated before the addition of the ethanol and ethyl acetate or before the second refluxing of the mixture but after the addition of ethanol and ethyl acetate. The last experiment was performed in order to make sure that the higher yields obtained where the alcohol was distilled off were not due at least in part to the greater ease of isolation of the ester.

The condensation of esters other than ethyl acetate with the formation of beta ketonic esters does not lend itself to a study of the relationship of structure to extent of reaction. It is possible to vary one group at a time only through the condensation of dissimilar molecules of ester and this makes possible the formation of two or three different beta ketonic esters in the reaction mixture, thus greatly increasing the difficulties of analysis. In the case of the 1,3-diketones a simple synthesis and alcoholysis is possible only when the ester concerned is incapable of condensation with itself, and the monoketone is of such a structure that it can condense with the ester to form only a single compound. The structures of dibenzoylmethane and its derivatives are such that only simple alcoholysis and synthesis are possible and so these diketones were selected as the basis of study. Broderick in 1927[5] showed that the percentage of diketone present in the reaction mixtures was the same irrespective of whether he started with dibenzoylmethane and alcohol or ethyl benzoate and acetophenone. However, this did not represent a true equilibrium point because of the separation of the solid salt of the diketone. An extensive search has been carried on since that time in order to discover an inert solvent in which homogeneity could be maintained during the synthesis or alcoholysis of a diketone. There has been found no inert solvent in which the sodium, potassium or lithium salt of a diketone was sufficiently soluble to permit determinations of the extent of alcoholysis or synthesis in the presence of a catalyst for the latter reaction. Attention was therefore directed toward the study of the relationship of structure to the rate of alcoholysis in the presence of hydrogen chloride,[6] and of sodium ethoxide.

There are several reasons why the relative rates of alcoholysis of 1,3-diketones cannot be determined and compared as accurately in the presence of sodium ethoxide as when hydrogen chloride is the catalyst. For example, the former reagent catalyzes "side reactions" such as the acetoacetic ester condensation. This may be minimized and it is believed practically eliminated through the use of a large molecular excess of alcohol. However, as may be seen from an inspection of the data shown in the figures, the ultimate percentage of alcoholysis, calculated on the amount of diketone used, is in many cases considerably less than 100%, this despite the fact that with the ratio of one mole of sodium ethoxide to two moles of acetylbenzoylmethane all of the diketone had disappeared after one hun-

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[5] Ph.D. Dissertation, University of Wisconsin, 1928.

[6] Adkins, Kutz and Coffman, THIS JOURNAL, 52, 3212 (1930).

dred hours. This failure to obtain a 100% recovery of ester is no doubt connected with the fact that it is impractical to determine how much ester is lost during the analysis, due to saponification or other reactions, as was done in the study of alcoholysis involving the use of hydrogen chloride. Perhaps the most serious obstacle to a precise comparison of the rates of alcoholysis of various diketones is the fact that they differ so greatly with respect to their sensitivity toward the catalyst. This makes it impossible to compare any considerable group of diketones or keto esters under identical experimental conditions.

The rates of alcoholysis at 60° of diacetylmethane, acetylbenzoylmethane, benzyldiacetylmethane, dibenzyldiacetylmethane, ethyldiacetylmethane, benzylacetylbenzoylmethane, ethyl acetoacetate, ethyl ethylacetoacetate, ethyl benzylacetoacetate, ethyl diethylacetoacetate and ethyl dibenzylacetoacetate were measured in ethanol in the presence of various amounts of sodium ethoxide. Approximately 0.01 mole of the diketone or keto ester with the desired amount of sodium ethoxide was dissolved in enough ethanol to make the volume of the reaction mixture 40 ml. The reaction was stopped after the alcoholysis had proceeded for the desired length of time by adding an excess of a normal solution of hydrogen chloride in ethanol. After shaking the mixture, 2 ml. of phenylhydrazine was added to combine with the excess hydrogen chloride and ketones. After standing for two or three hours the ester was distilled out and determined as described in our previous paper. In only one case was any modification of this procedure necessary. Ethyl ethylacetoacetate gave ethyl butyrate as well as ethyl acetate upon alcoholysis so that two 20-ml. portions of propanol were added and distilled out after the normal distillation procedure had been followed.

Diacetylmethane, acetylbenzoylmethane, ethyldiacetylmethane, benzyldiacetylmethane, dibenzyldiacetylmethane and benzylacetylbenzoylmethane were prepared and had the physical constants described in a previous paper. Acetoacetic ester was dried over calcium chloride and fractionated from the commercial products, b. p. 85–87° (25 mm.), d_{25}^{25} 1.012. Ethyl ethylacetoacetate was prepared from acetoacetic ester, using toluene as a medium; the yield was 60% of product boiling at 100–102° (25 mm.), d_{25}^{25} 0.9690. Ethyl diethylacetoacetate was prepared from the monoethyl compound, the yield being 40 to 50%; b. p. 115–117° (25 mm.), d_{25}^{25} 0.9435.[7] Ethyl benzylacetoacetate was obtained in a 58% yield, b. p. 165–170° (25 mm.), d_{25}^{25} 1.050.[8] The ethyl dibenzylacetoacetate after crystallization from ethanol had a melting point of 56–57°.[9] Diethyldibenzoylmethane was prepared in a yield of 35% through the re-

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[7] Wislicenus, Ber., ?, 683 (1874).

[8] Ehrlich, *Ann.*, 187, 12 (1877).

[9] Fittig and Christ, *ibid.*, 268, 123 (1891).

action of diethyl malonyl dichloride with benzene in the presence of aluminum chloride. The diketone melted at 102–103°.[10]

The rate of alcoholysis of five beta ketonic esters and six 1,3-diketones for various concentrations of sodium ethoxide is shown in Figs. 1, 2 and 3. The molar ratio of sodium ethoxide to diketone or keto ester is shown in parentheses for each curve. The rate of alcoholysis of diacetylmethane and acetylbenzoylmethane was increased by almost 100% when the ratio of sodium ethoxide to diketone was increased from 1:5 to 1:2. A further increase to a ratio of 1:1 brought about what was apparently a small decrease in the rate of alcoholysis but it is believed that this was due to the greater loss in ethyl acetate prior to analysis rather than to a real decrease in the rate of alcoholysis.

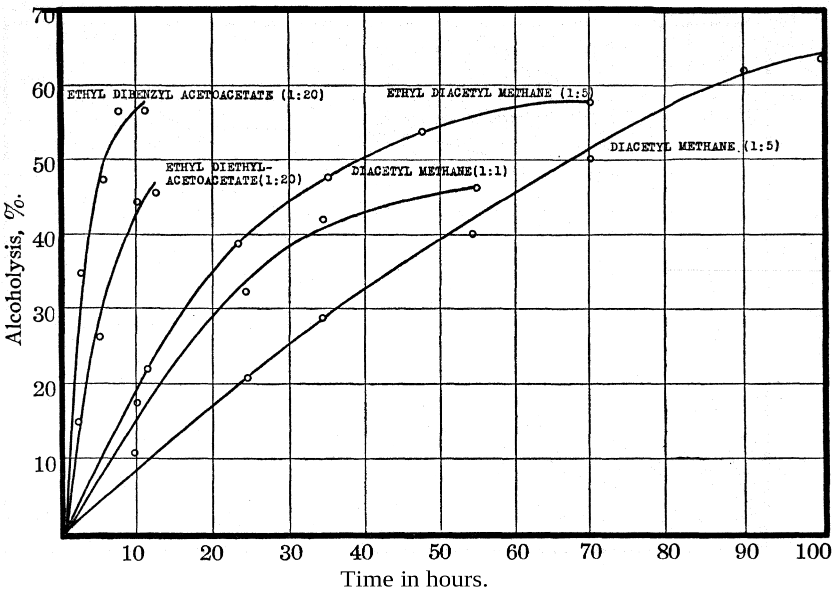

Fig. 1.—Rates of alcoholysis of various 1,3-diketones and β-keto esters. The molecular ratio of sodium ethoxide to dicarbonyl compound is shown in parentheses for each curve.

There was very little difference between the rates of alcoholysis of diacetylmethane and acetylbenzoylmethane irrespective of whether the comparison was made at a ratio of sodium ethoxide to diketone of 1:5 or 1:2.

The keto esters undergo alcoholysis more slowly, for a given ratio of keto compound to sodium ethoxide, than do the 1,3-diketones. This is true irrespective of whether the comparison is made between the unsubstituted compounds or between those in which one or more substitutions have been made on the carbon atom between the carbonyl groups.

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[10] Freund and Fleischer, *Ann.*, 373,296 (1910).

Substitution of ethyl or benzyl groups on the carbon atom between the carbonyl groups greatly increases the rate of alcoholysis of both keto esters and diketones for a given ratio of keto compound to sodium ethoxide. This may be expressed in another way by saying that it is feasible to cleave a monosubstituted compound, within a given period, with a very much lower ratio of sodium ethoxide to keto compound than is possible in the case of the parent substance. In the case of the disubstituted compounds the rate of alcoholysis is relatively very rapid even where there is only one mole of sodium ethoxide for twenty moles of dicarbonyl compound. However, even a qualitative comparison is perhaps not justifiable, for in the case of the unsubstituted and of the monosubstituted compounds there is the probability that a very considerable portion of the sodium ethoxide reacts with the enol and is thus eliminated as a catalyst. There is no possibility of this in the case of the disubstituted dicarbonyl compounds unless enolization occurs by the migration of a hydrogen from the methyl group at the end of the molecule. Even this is not possible for diethyldibenzoylmethane, which readily undergoes alkaline alcoholysis and hydrolysis.

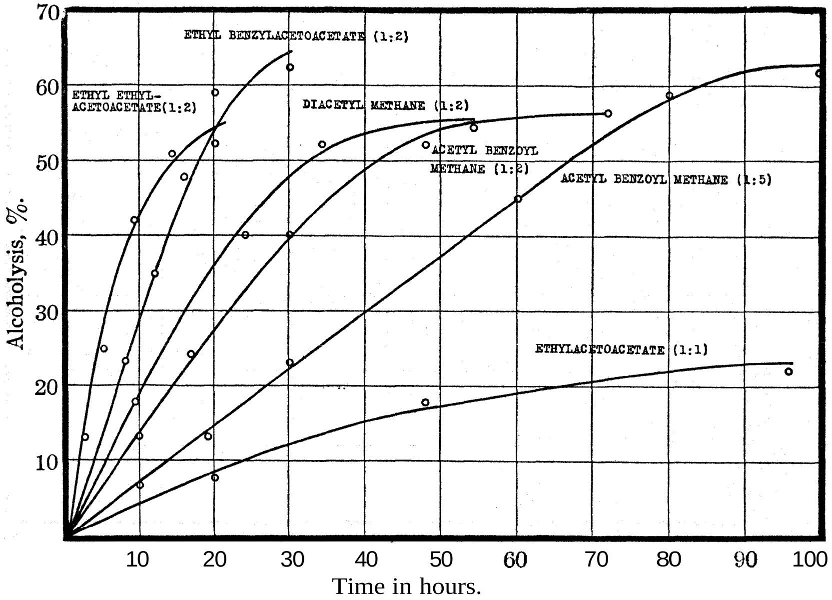

Fig. 2.—Rates of alcoholysis of various 1.3-diketones and β-keto esters. The molecular ratio of sodium ethoxide to dicarbonyl compound is shown in parentheses for each curve.

Two grams of this diketone dissolved in 50 ml. of ethanol was allowed to undergo alcoholysis at 60° for twelve hours in the presence of an equimolecular amount of sodium ethoxide. Acidification with 50 ml. of dilute aqueous hydrochloric acid did not give a crystalline precipitate and it was considered that the diketone had been completely split into ethyl benzoate and the corresponding monoketone. The reaction mixture was then made alkaline with solid sodium hydroxide and the ester saponified. After evaporation to dryness, the residue was dissolved in 200 ml. of water and washed with ether. Evaporation of the water solution to a small volume, acidification with hydrochloric acid and cooling precipitated out 0.819 or 94% of the theoretical amount of benzoic acid. One and four-tenths grams of diethyldibenzoylmethane was hydrolyzed at 60° for ten hours in 75 ml. of a 1% solution of sodium hydroxide in 80% ethanol. After evaporation to dryness, the residue was dissolved in 200 ml. of water, washed with ether and 0.5960 g. of benzoic acid precipitated with sulfuric acid. The yield was thus 98% of the theoretical.

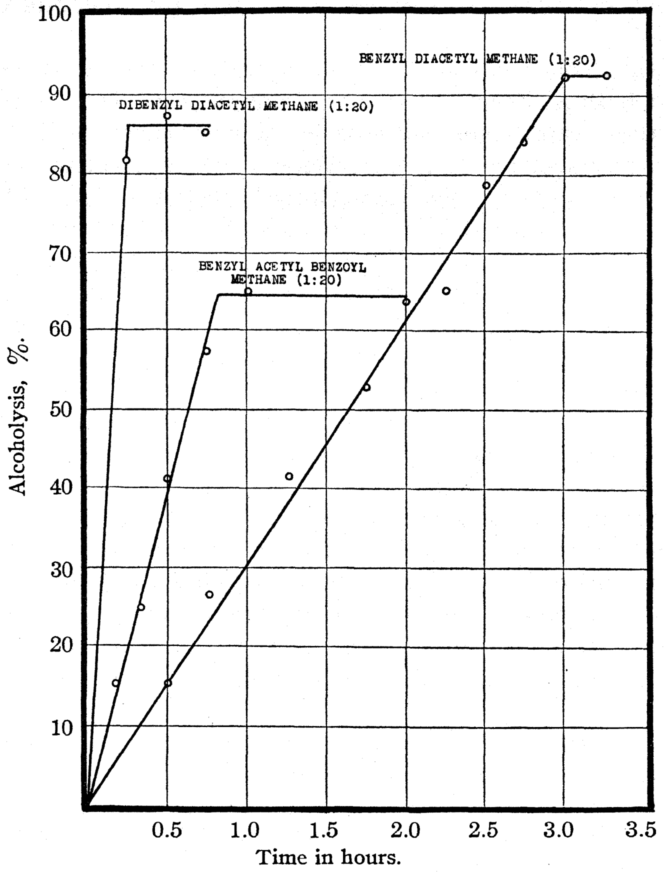

Fig. 3.—Rates of alcoholysis of three 1,3-diketones.

The high reactivity of the substituted keto esters in alkaline alcoholysis as compared with the unsubstituted esters is in accord with the qualitative experiments of Dieckmann[11] on the cleavage of substituted acetoacetic esters. However, his inference from these experiments with regard to the concentration at equilibrium of acetoacetic ester and its derivatives is unjustified by any experimental work, and in so far as it applies to the non-condensation of isobutyric ester has been shown by McElvain to be incorrect.

The rate of alcoholysis of six of the diketones has been determined in the presence of both hydrogen chloride and sodium ethoxide. As previously reported, these compounds in the order of decreasing reactivity are as follows: diacetylmethane, ethyldiacetylmethane, acetylbenzoylmethane, benzoyldiacetylmethane, benzylacetylbenzoylmethane and dibenzyldiacetylmethane. This is also the order of reactivity (with one exception) of the diketones with respect to sodium ethoxide except that it is one of increasing reactivity. The exception to this statement is acetylbenzoylmethane, which is slightly less reactive in the presence of sodium ethoxide than would be expected on the basis of its reactivity in the presence of hydrogen chloride. There can be no doubt that in general this reversal of reactivity with respect to the two conditions of alcoholysis holds true and that the differences in reactivity are quite large. For example, taking the end members of the series referred to above, it was found that in the presence of hydrogen chloride, diacetylmethane was in the vicinity of ten times as reactive as its dibenzyl derivative, while in the presence of sodium ethoxide the dibenzyl derivative was one or two hundred times as reactive as the parent substance. A similar comparison cannot be made for the keto esters because experimental conditions have not as yet been found in which these compounds undergo alcoholysis in the presence of hydrogen chloride.

It was previously pointed out that there seemed to be a parallelism between the extent of enolization of a 1,3-diketone and its reactivity toward alcoholysis in the presence of hydrogen chloride. Since the order of reactivity of the 1,3-diketones is the opposite in alkaline alcoholysis to that in acid alcoholysis, it seems reasonable to consider this as evidence in support of the hypothesis of Bradley and Robinson that the cleavage of diketones in alkaline medium takes place through the keto rather than the enol compound. This view is also in accord with the very high reactivity in alkaline alcoholysis of the disubstituted 1,3-diketones and keto esters which are incapable of enolization. It is quite possible that cleavage also occurs through the enol compound since Fieser[12] has shown that a fixed enol of a 1,3-diketone readily undergoes cleavage.

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[11] Dieckmann, *Ber.*, **33,** 2678 (1900).

[12] Fieser, THIS JOURNAL, 51, 940 (1929).

Summary

It has been shown that the amount of acetoacetic ester to be obtained from the reaction mixture is the same irrespective of whether it is synthesized from ethyl acetate and sodium ethoxide or remains from the alcoholysis of an amount of acetoacetic ester molecularly equivalent to the amount of sodium ethoxide used in the synthetic reaction. All attempts to make similar determinations on the synthesis and alcoholysis of 1,3-diketones have failed because no conditions have been found under which homogeneity would be maintained during the synthesis and alcoholysis.

The rates of alcoholysis of six 1,3-diketones and five beta keto esters have been determined at 60° in the presence of various ratios of sodium ethoxide. The keto esters were found to be more stable than the diketones toward alcoholysis for a given ratio of sodium ethoxide. Substitution on the carbon atom between the two carbonyl groups very considerably increased the rate of alcoholysis in the presence of sodium ethoxide. This effect reached its maximum in the case of the diacyl dialkyl methanes, which underwent alcoholysis hundreds of times as rapidly as the diacyl methanes.

When the six diketones whose reactivity was measured in the presence of both hydrogen chloride and sodium ethoxide were arranged in the order of decreasing reactivity with respect to alcoholysis in the presence of hydrogen chloride, they were found to be arranged (with one exception) in the order of increasing reactivity toward alcoholysis in the presence of sodium ethoxide. Diethyldibenzoylmethane, which is incapable of enolization, readily underwent alkaline alcoholysis and hydrolysis. These facts taken in conjunction with the parallelism between extent of enolization and rate of acid alcoholysis offer support to the hypothesis of Bradley and Robinson that alkaline cleavage of 1,3-diketones takes place through the reaction of the carbonyl rather than of the enol form of the diketone.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE MOLECULAR WEIGHT OF COCOSIN

BY BERTIL SJÖGREN AND ROMUALD SPYCHALSKI

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The oil-seed globulins, edestin,[1] amandin[2] and excelsin,[2] as well as the other vegetable proteins, legumin,[3] *r*-phycocyan,[4,5] *r*-phycoerythrin[4,5] and *c*-phycocyan,[5] so far studied in this Laboratory by means of ultracentrifugal analysis, have all proved to be monodisperse and to belong to the fourth group of proteins, having a molecular weight of about 208,000, that is, approximately six times the weight of ovalbumin.6 They were found to be very stable, but with a tendency to dissociate into lower multiples of 34,500 at higher PH values.[6]

In order to get more information concerning this large class of proteins, we took up the coconut globulin, in the following called cocosin,[7] for an ultracentrifugal examination. In chemical composition cocosin resembles excelsin very much, both having a high sulfur content, slightly exceeding 1%. With respect to solubility cocosin and edestin are almost identical, in so far as high salt concentrations are necessary to hold them in solution. Cocosin is obtained in a definite crystalline state, which may be taken as an indication of its homogeneity. Therefore the result arrived at was quite surprising: the protein was easily decomposed during the preparation and gave an unstable and polydisperse product.

Preparation of Material.—The nuts were freed from shells and skins, then ground in a mill to a fine paste (340 g.) and suspended in 10% sodium chloride solution (3000 cc.). Enough toluene was added to serve both as a preservative and as a solvent for the fat. The mixture was digested with stirring at room temperature for twenty-four hours. A test showed that no more protein could be extracted after this treatment. The bulk of the insoluble part was removed by means of a cloth filter. The solution was further freed from suspended particles and from oil and fat partly dissolved in the toluene by filtering and centrifuging. Saturated ammonium sulfate solution was then added to 60% saturation. After standing for one day at 5° the precipitate was filtered off and washed with half-saturated ammonium sulfate solution. The protein precipitate was dissolved in phosphate buffer of *PH* 6.7 (0.033 *M* in KH_2PO_4 and 0.033 M in Na_2HPO_4), containing 7% of sodium chloride. This high *PH* and salt content was used in order to increase the solubility. The solution was then dialyzed in the ice box for six days against the same buffer; volume of solution, 20 cc.; concentration, 3.05% (Ma-

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T. Svedberg and A. J. Stamm, THIS JOURNAL, 51, 2170 (1929).

[2] T. Svedberg and B. Sjögren, *ibid.*, 52, 279 (1930).

[3] T. Svedberg and B. Sjögren, *ibid.*, 52, 3279 (1930).

[4] T. Svedberg and N. B. Lewis, *ibid.*, 50, 525 (1928).

[5] T. Svedberg and T. Katsurai, *ibid.*, 51, 3573 (1929).

[6] T. Svedberg, *Kolloid-Z.*, 51, 10 (1930).

[7] Compare T. B. Osborne, "Vegetable Proteins," Longmans, Green and Co., London, 1916, pp. 57, 78.

terial I). The substance was comparatively homogeneous, consisting principally of one component.

It may be mentioned that the above method of preparation was used for preparing another batch of cocosin, the final product, however, being dissolved in 10% sodium chloride solution. This material was very non-homogeneous, breaking up more and more with time. The same result was obtained when coconut meal was used instead of the fresh nuts.

Before carrying out these preparations we also made an attempt to get the protein in a pure state by dialyzing the solution against water after precipitation with ammonium sulfate and dissolving in 10% sodium chloride. When working with proteins we have often had the opportunity to observe that some of them, and especially the oil-seed globulin, are very sensitive to long water dialysis. Hydrolysis and denaturation then occur. Cocosin showed this phenomenon in a pronounced way, the crystallized cocosin material prepared by dialysis against water proving to be very difficult to bring into solution. By centrifugal analysis this material was found to be quite decomposed.

To avoid these difficulties, especially the using of high salt contents, which complicates the centrifugal analysis, we modified the method in the following way. After precipitation with crystallized ammonium sulfate to 60% saturation, the globulin was dissolved in 5% sodium chloride solution. Hereafter, in order to increase the solubility, Na_2HPO_4 was added to a concentration of 0.017 M. Then, before a second precipitation, the P_H of the solution was decreased to 5.5 by means of KH_2PO_4. This brought about no change in the precipitation limits. After treatment as before, cocosin was completely dissolved in Na_2HPO_4 (0.2 M) and dialyzed against the same solvent for six days. From 700 g. of coconut paste we derived 30 cc. of solution containing 0.99% cocosin (Material II). The protein was found to be a mixture of two components.

In our last attempt to prepare cocosin we worked as quickly as possible, also using the simplest method of purification. After digesting the paste (340 g.) and precipitating once as in the case of Material I, the product was dissolved in phosphate buffer of P_H 6.7 (0.033 M in KH_2PO_4 and 0.033 M in Na_2HPO_4), containing also 4% of sodium chloride, and dialyzed against the same buffer in the ice box for five days; volume of solution, 50 cc.; concentration, 0.74% (Material III). This substance was also a mixture of two molecular species.

Specific Volume and Light Absorption.—For both these measurements Material III was used at a P_H of 6.7 with solvent as above.

The partial specific volume was determined pycnometrically at 20.2°. Two determinations at different concentrations gave the mean value 0.746 in agreement with the values obtained for the other proteins which follow the law of simple multiples.

The light absorption was studied by means of the Judd-Lewis spectrophotometer as described in earlier communications. The protein concentrations were 0.15 and 0.074% with a thickness of layer 2.0 cm. The absorption maximum $\epsilon/c = 7.0$ was situated at 280 $m\mu$, and the minimum $\epsilon/c = 2.7$ at 255 $m\mu$. The absorption curve is given in Fig. 1.

Determination of Sedimentation Constant and Different Molecular Components.—The runs were carried out with the high-speed oil-turbine ultracentrifuge. In the case of Material I the speed was 23,000, in the other runs about 43,000, r. p. m. The time varied from two to three and one-half hours, the temperature during each run from 20 to 23°, other experimental conditions being as usual.

The sedimentation constant is given by $s = (dx/dt) \times 1/(0^2x)$, where x is the distance from axis of rotation, ω the angular velocity and t the time. In cases of non-homogeneous material the amounts of the different molecular species may be calculated from their sedimentation and diffusion constants, reducing the galvanometer deflections of the microphotometer curves to represent relative concentrations.[1,2,4] The centrifugal force must be large enough to give a marked separation of the components. Thus, at the highest possible speed, *viz.*, 45,000 r. p. m., giving a centrifugal force of about 120,000 times that of gravity, it is easy to observe a component of weight 6 × 34,500 in mixture with a substance of molecular weight 3, 2 or 1 X 34,500. It is also possible to distinguish a component of 104,000 from one of 34,500 but not from one of 68,000, without using a very long time of centrifuging. Owing to the difficulties of taking into account the difference in light absorption between the normal and the decomposed product, the calculations of the relative amounts of the components should only be regarded as an approximation.

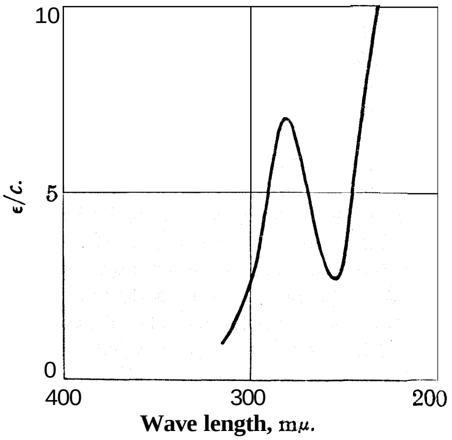

Fig. 1.—Light absorption of cocosin.

In Table I the determinations with the Materials I, II and III are summarized. The other preparations gave such unstable products that we refrain from mentioning the values obtained.

TABLE I

COCOSIN, SUMMARY OP SEDIMENTATION VELOCITY MEASUREMENTS

Subs.	Solvent KH$_2$PO$_4$, M	Na$_2$HPO$_4$, M	NaCl, %	P$_H$ of soln.	Concn. of protein	$s_{20°} \times 10^{13}$	State of soln.
Material I	0.033	0.033	4.7	6.7	0.30	10.47 corr. value 12.4	
Material I	.013	.053	2.4	7.4	1.30	11.37	
Material II	..	.200	...	7.9	0.20	...	[c]
Material III	.033	.033	4.0	6.7	.37	...	[d]
Material III	,030	.030	3.6[a]	9.7	.13	...	[e]
Material III	.015	.035	...	11.8	.37	9.71	[f]

[a] 0.033 M in NaOH. [b] 0.067 M in NaOH. [c] Mixture of approximately 65% molecules of weight 208,000 and 35% of weight 104,000. [d] Mixture of approx. 75% 208,000, 25% 104,000. [e] Mixture of approximately 50% 208,000, 50% 104,000. [f] Decomposed; 15% non-centrifugible products.

As may be seen from the table, Material I was almost homogeneous, giving a value of s quite in agreement with the values obtained for the other proteins possessing a molecular weight of 208,000. A small amount of a lighter component was present.

There were at least two molecular species present in Material II. The stock solution was a mixture of about 65% molecules of weight 208,000 and 35% of weight 104,000. Assuming the cocosin molecule to be of weight 208,000, then the presence of the smaller component can be considered as the first stage of the protein cleavage, caused by the high PH. This splitting-up of the molecule with increasing PH has in earlier cases, as a rule, been found to be reversible. Thus if the PH of the solution is brought back to a value lying in the stability region, one would expect a monodisperse product. The stock solution of Material II was dialyzed against a phosphate buffer of PH 6.0 (0.17 *M* in KH_2PO_4 and 0.03 *M* in Na_2HPO_4, containing 4% of sodium chloride) for five days. By a second analysis we found that the amount of the smaller component had decreased. In order to complete the reaction in this direction the dialysis was continued for six days more. During this treatment the cocosin was, however, totally decomposed which behavior is in line with the former experience on the high sensitivity of the oil-seed globulins to prolonged dialysis.

Material III proved to be somewhat more homogeneous in so far as the stock solution had approximately a composition of 75% molecules of weight 208,000 and 25% of weight 104,000. In more alkaline solutions the protein was broken up into units of one-half the normal molecular weight and at still higher PH values into particles of unequal size. A run was also made at a PH of 5.5, using phosphate buffer and 9% sodium chloride, which confirmed the result obtained at PH 6.7. Because of the very high salt content, involving great corrections, the values are not reproduced here.

Determination of Molecular Weight.—For the sedimentation–equilibrium method, 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 c_1 and c_2 are the concentrations at the distances x_1 and x_2 from the center of rotation, R the gas constant, T the absolute temperature, V the partial specific volume of the solute, p the density of the solvent and w the angular velocity.

Two runs were made with Material III at PH 6.7 using the same buffer as before and the concentration 0.15%. In Fig. 2 the values of the molecular weight are plotted against the distance from the center of rotation. As may be seen from the diagram the material was non-homogeneous with regard to molecular weight, giving values from approximately 215,000 down to 110,000 with the higher values all lying around 208,000. As the time between the two runs was nearly a week, the slight difference observed may be interpreted as a further splitting-up of the cocosin.

The results of our measurements make it extremely probable that normal native cocosin has a molecular weight of the same magnitude as the other oil-seed globulins so far analyzed, *viz.*, six times the weight of ovalbumin or 208,000. Their molecules are all spherical with a molecular radius of about $3.95\ m\mu$. The component with a molecular weight half that of the normal present in the cocosin samples studied may be considered as the first decomposition product of the protein cleavage.

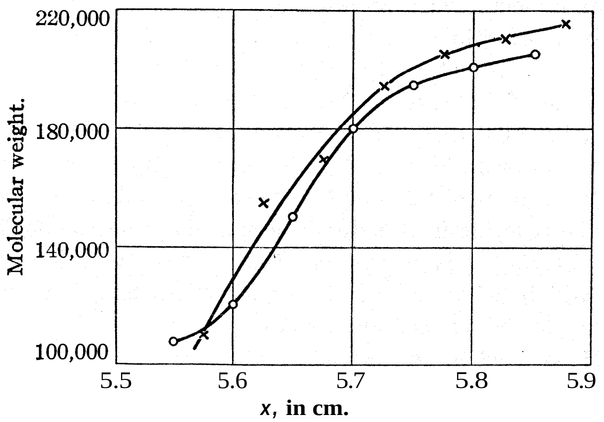

Fig. 2.—Variation of molecular weight with distance from axis of rotation: —X—. Run 1; —O— Run 2, one week later.

The expenses connected with this work have been defrayed by a grant from the foundation "Therese och Johan Anderssons Minne."

Summary

1. By means of ultracentrifugal methods an attempt was made to determine the molecular weight of the coconut globulin, called cocosin.

2. This protein was found to be rather unstable, being easily decomposed during the process of preparation.

3. The centrifugal analysis proved cocosin to be a mixture of two main components of weight about 208,000 and 104,000 with the larger molecules present in much greater amounts than the smaller ones.

4. It was considered as extremely probable that native cocosin has a molecular weight within experimental limits identical with the other oil-seed globulins earlier studied, *viz.*, 208,000, and that the small fraction present of weight half of this normal molecule represents the first stage of the protein cleavage.

UPSALA, SWEDEN

[Contribution from the Chemical Department, Birkbeck College, University of London]

UNSATURATION PHENOMENA OF ACETYLENIC ACIDS AND ESTERS.
III. THE CONSTITUTION OF SOME MERCURY DERIVATIVES

By William Whalley Myddleton, Arthur W. Barrett and John H. Seager

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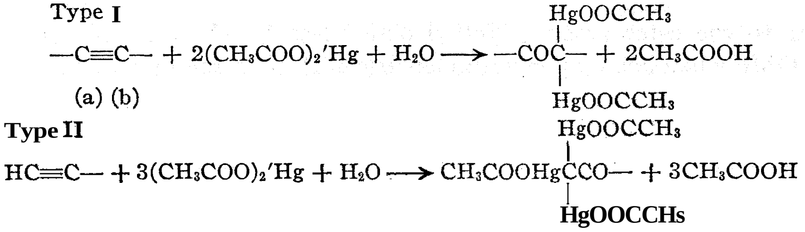
Earlier communications published from these Laboratories[1] described the isolation of mercury derivatives formed by the action of mercuric acetate upon various acetylenic acids and esters in acetic acid solution. The acetylenic compounds employed were of two types: I, $CH_3(CH_2)'_mC\equiv C(CH_2)'_nCOOR$, where R is alkyl or hydrogen and where the values of m and n were

$m = 0, n = 7$ in 9–10 undecinoic acid
$m = 7, n = 7$ in stearolic acid
$m = 7, n = 11$ in behenolic acid

and II, $HC\equiv C(CH_2)'_nCOOR$, where $n = 8$ in 10,11-undecinoic acid.

The mode of formation and the composition of the mercury compounds as well as the nature of the products derived from them by decomposition with hydrochloric acid were in accord with the following interpretation of the action of mercuric acetate upon the acetylenic linkage.



Type I

$$-C\equiv C- + 2(CH_3COO)_2'Hg + H_2O \longrightarrow -CO\overset{HgOOCCH_3}{\underset{HgOOCCH_3}{C}}- + 2CH_3COOH$$

(a) (b)

Type II

$$HC\equiv C- + 3(CH_3COO)_2'Hg + H_2O \longrightarrow CH_3COOHg\overset{HgOOCCH_3}{\underset{HgOOCCHs}{C}}CO- + 3CH_3COOH$$

In Type II the acetylenic hydrogen atom is substituted while the usual addition takes place at the triple bond.

During decomposition of the mercury compounds with hydrochloric acid, each acetoxymercuri group was assumed to be replaced by hydrogen with formation of a ketonic compound free from mercury. In the case of 9,10-undecinoic acid (Type I) and its ethyl ester, two isomeric ketonic derivatives were isolated, thus establishing an alternative reaction in which the acetoxymercuri groups were added to the carbon atom (a) and the oxygen atom to (b) in the equation given above.

The present communication describes further investigations upon the constitution of the mercury compounds.

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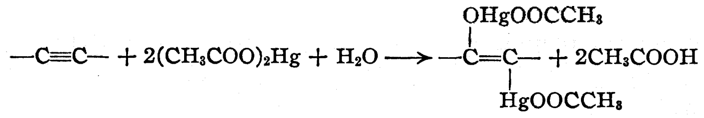
[1] (a) Myddleton and Barrett This Journal, 49, 2258 (1927); (b) Myddleton, Berchem and Barrett, *ibid.*, 49, 2264 (1927)

Mercuration of Acetylenic Compounds of Type I

In the mercury derivatives from esters of Type I there appeared to be a difference in reactivity of the two mercury atoms toward caustic alkalies and hydrogen sulfide but this could not be established by the isolation of pure products from these reactions. An alternative constitution was therefore tentatively assigned to the mercury derivatives to account for a difference in reactivity of the mercury groups and evidence of this constitution was sought and discovered in other directions. The alternative constitution was derived from the following interpretation of the action of mercuric acetate upon the acetylenic bond.



$$-C\equiv C- + 2(CH_3COO)_2Hg + H_2O \longrightarrow -\overset{\overset{\displaystyle OHgOOCCH_3}{|}}{C}=\underset{\underset{\displaystyle HgOOCCH_3}{|}}{C}- + 2CH_3COOH$$

The resulting mercury derivative is unsaturated and the first action of hydrochloric acid in causing the replacement of acetoxymercuri groups by hydrogen would be to yield an enolic product containing the group $-C(OH)=CH-$. Rapid transformation to the ketonic form might be anticipated under the influence of the mineral acid. Indeed no signs of an enolic form were discovered during the decomposition of the mercury derivatives already described. The most favorable conditions for observing the intermediate formation of an enolic derivative were sought by choosing an acetylenic ester with a shorter carbon chain and with the acetylenic bond near to the ester group. Methyl octine-1-carboxylate $CH_3(CH_2)_5C\equiv C-COOMe$ when acted upon with mercuric acetate in the manner previously described gave a mercury derivative analyzing in accordance with the composition $CH_3(CH_2)_5C(OHgOOCCH_3)=C(HgOOCCH_3)COOMe$.

The decomposition of this compound with concentrated hydrochloric acid gave an ester which, as soon as liberated, gave a deep violet coloration with ferric chloride in alcoholic solution, indicating the presence of an enolic form. Analysis of the ester by the method of Kurt Meyer[2] indicated the presence of 13.5% of the enolic form.

The mercury derivative was very slightly soluble in hot alcohol and when the cooled solution was mixed with two drops of a neutral aqueous solution of ferric chloride it gave in about one minute a faint reddish-violet coloration indicating an enolic structure. In this reaction there is a direct replacement of an acetoxymercuri group by iron to give the colored ferric salt of an enolic compound. To facilitate this reaction a mercury derivative more soluble in alcohol was sought by introducing a phenyl group into the acetylene. Ethyl phenylpropiolate $C_6H_5C\equiv CCOOEt$ gave a mercury derivative melting with decomposition at 192° and analyzing in agreement with the composition $C_6H_5C(OHgOOCCH_3)=C(HgOOCCH_3)COOEt$. It was

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[2] K. Meyer, Ber., 44, 2718 (1911).

readily soluble in hot alcohol and moderately soluble in cold. The cold alcoholic solution gave in a few seconds a deep reddish-violet coloration with two drops of aqueous ferric chloride. The ester liberated from the mercury derivative by the action of hydrochloric acid gave a similar coloration and was shown by Kurt Meyer's method to contain 20% of the enolic form an hour after isolation.

The Action of Halogens on the Mercury Derivatives.—As a means of further distinguishing between the two structures $—COC(HgOOCCH_3)_2—$ and $—C(OHgOOCCH_3)=C(HgOOCCH_3)—$ the action of halogens was investigated. In the first case chlorine would be expected to produce a dichloro ketone by causing the replacement of each acetoxymercuri group by a chlorine atom; in the second case a monochloro ketone would result through the intermediate formation of $—C(OCl)=CCl—$ which after hydrolysis in the aqueous acid used in the isolation would lead to $—C(OH)=CCl—$ and finally the ketonic form $—COCHCl—$.

The mercury derivatives prepared from stearolic acid and behenolic acid were made to react with chlorine and with bromine in refined petroleum ether, in chloroform and in glacial acetic acid. Mono-halogen ketonic acids were formed quantitatively. The mercury derivatives from methyl octine-1-carboxylate and from ethyl phenylpropiolate gave dibromo ketonic esters when decomposed with bromine. As in the last two instances the mercury derivatives developed a violet coloration in contact with alcoholic ferric chloride, it cannot be assumed that the formation of a dibromo ketonic ester is evidence that two mercury atoms are attached to one carbon atom. To reconcile the two reactions it is necessary to assume that during treatment with bromine the following changes take place.

$$—C(OHgOOCCH_3)=C(HgOOCCH_3)— \xrightarrow{+Br_2} —C(OBr)=CBr— \xrightarrow{+Br_2}$$
$$—C(OBr)BrCBr_2— \xrightarrow{-Br_2} —COCBr_2—$$

The dibromo ketonic ester prepared in this way from ethyl phenylpropiolate gives the theoretical yield of benzoic acid after hydrolysis with a semi-normal alcoholic solution of potassium hydroxide, thus proving that when mercuric acetate acts upon ethyl phenylpropiolate under the stated conditions the mercury groups enter the side chain exclusively. Phenylpropiolic acid is also mercurated exclusively in the side chain and the derivative formed yields with bromine benzoyl dibromo-acetic acid, which is recovered as w-dibromo-acetophenone after loss of carbon dioxide.

Mercuration of Acetylenic Compounds of Type II

The following acetylenic compounds containing the group $HC\equiv C—$ were converted into mercury derivatives by the action of mercuric acetate in acetic acid solution.

$HC\equiv C(CH_2)_2COOH$	10.11-undecinoic acid
$CH_3(CH_2)_4C\equiv CH$	Heptine-1
$CH_3(CH_2)_5C\equiv CH$	Octine-1
$C_6H_5C\equiv CH$	Phenylacetylene

The analysis of the products indicates the presence of three acetoxymercuri groups, and methyl ketones are formed by decomposition with hydrochloric acid.

The mercury derivative from phenylacetylene cannot be decomposed with bromine at a temperature sufficiently low to yield a simple product, but the other derivatives examined gave tribromo ketones with bromine in the form of non-crystallizable oils. Since they give bromoform when they are decomposed with caustic alkalies, it is necessary to assume that during mercuration the acetylenic hydrogen is replaced by an acetoxymercuri group.

It is possible to formulate the behavior of these mercury derivatives on the assumption that they possess a constitution similar to those derived from acetylenic compounds of Type I, namely, $—C(OHgOOCCH_3)=C(HgOOCCH_3)_2$, although no evidence has been obtained of unsaturation or of the formation of enolic compounds during decomposition with acids. They do not for example develop any coloration with ferric chloride in alcohol, but this of course may be due to their insolubility.

The decompositions of these derivatives with hydrochloric acid and with bromine may be accounted for as follows

$$—C(OHgOOCCH_3)=C(HgOOCCH_3)_2 \xrightarrow{HCl} —C(OH)=CH_2 \longrightarrow —COCH_3$$

$$—C(OHgOOCCH_3)=C(HgOOCCH_3)_2 \xrightarrow{Br_2} —C(OBr)=CBr_2 \xrightarrow{Br_2}$$

$$—C(OBr)BrCBr_3 \xrightarrow{-Br_2} —COCBr_3$$

Experimental Part

The Action of Mercuric Acetate on Acetylenic Compounds.—The preparation of mercury derivatives of acetylenic compounds by the action of mercuric acetate was carried out under the conditions described in a previous communication.[1b]

When the acetylenic compound contains the group $HC\equiv C—$, it was found desirable to moderate the reaction by dissolving the mercuric oxide in hot acetic acid and then cooling to crystallize some mercuric acetate before adding the acetylene slowly. Under other conditions the heat evolved was sufficient to cause the formation of much mercurous acetate and even free mercury by reduction. Further experience in the preparation of these mercury derivatives has shown that they sometimes separate as viscous oils when the acetic acid solution is diluted with water. Such oily products may be converted into a microcrystalline powder by triturating with alcohol and then with ether.

Analysis of the Mercury Derivatives.—Mercury was determined by the destructive hydrogenation method of H. ter Meulen.[3] Other analyses were carried out as described in the earlier communication.[1a] The following results were obtained.

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[3] H. ter Meulen, Rec. *trav. chim.*, 45, 368 (1926).

	Analysis of Hg derivative		
Acetylenic compd.	Hg, %	CH_3COO, %	Yield of ketonic compd. after dromp, with HCl, %
Methyloctine carboxylate	56.1	16.75	24.0
Calcd. for $C_{14}H_{22}O_7Hg_2$	57.0	16.78	26.45
Ethyl phenylpropiolate	56.46		26.6
Calcd. for $C_{15}H_{16}O_7Hg_2$	56.56		27.07
Heptine-1	67.8	20.1	13.0
Calcd. for $C_{13}H_{20}H_7Hg_3$	67.6	19.93	12.84
Octine-1	66.5	19.5	14.0
Calcd. for $C_{14}H_{22}O_7Hg_3$	66.6	19.6	14.13
Phenylacetylene	66.9	19.1	
Calcd. for $C_{14}H_{14}O_7Hg_3$	67.17	19.8	
Phenylpropiolic acid	64.5	15.0	
Calcd. for $C_{13}H_{11}O_7Hg_{2.5}$	64.24	15.12	

Decomposition of the Mercury Derivatives with Hydrochloric Acid.—The mercury derivative of methyl octine carboxylate was suspended in water and decomposed by adding concd. hydrochloric acid. The oily ester liberated was extracted with light petroleum, the extract washed, dried and evaporated. From 50 g. of material was obtained 12 g. of methyl β-keto-nonoate, b. p. 137.5° (28 mm.). By dissolving in alcohol and adding cupric acetate, the green copper salt was obtained, melting after recrystallization from benzene at 99°. The ester gave a deep violet coloration with ferric chloride in alcohol and a determination by the method of Kurt Meyer[2] showed the presence of 13.5% of the enolic form one hour after isolation.

A quantity of the ester was allowed to stand in contact with concd. hydrochloric acid for two days at room temperature. A mass of crystalline lamellae formed. After washing with water and recrystallization from light petroleum, these crystals of β-keto-nonoic acid melted at 70.5' and decomposed just above this temperature, losing carbon dioxide and forming methyl hexyl ketone, b. p. 171° (760 mm.); semicarbazone, m. p. 123". The semicarbazone mixed with the semicarbazone of authentic methyl hexyl ketone melted at 123°. The mercury derivative of heptine-1 gave with hydrochloric acid almost theoretical yields of methyl n-amyl ketone, b. p. 150° (760 mm.); semicarbazone, m. p. 123°, unchanged by admixture with semicarbazone of authentic methyl n-amyl ketone. It will be noted that this semicarbazone melts at the same temperature as that of methyl n-hexyl ketone.

The mercury derivative of octine gave methyl n-hexyl ketone, identified by the characteristics described above.

The mercury derivatives from phenylacetylene and phenylpropiolic acid gave with hydrochloric acid acetophenone, b. p. 200" (760 mm.). The semicarbazone melted when slowly heated between 188–190°, and when heated rapidly at 201°. The semicarbazone of authentic acetophenone behaved similarly. The oxime melted at 59°.

Decomposition of the Mercury Derivatives with Halogens.—The reaction between the mercury derivatives and halogens was found to proceed best in chloroform. In carbon tetrachloride the reaction was slower and in acetic acid was complicated by contamination of the halogen derivative with halogen-free ketonic compounds. By varying the water content of the acetic acid this complication was found to be due to the hydrolysis of the halogen followed by the action of the halogen hydracid thus formed on the mercury compound. Refined light petroleum was also an effective medium.

The mercury derivatives were suspended in the solvent and the halogen added slowly. In most cases it was necessary to warm the mixture in a water-bath at 40° during addition of the halogen. When excess was present the mixture was allowed to stand for several hours. The precipitate was filtered off and the solution washed repeatedly with water acidified with hydrochloric acid, and finally with distilled water. It was then dried over anhydrous sodium sulfate and evaporated. In some cases it was found possible to distil the halogen derivative under diminished pressure without decomposition and in these cases the boiling point is recorded in the table below.

Mercury derivative from	Halogen derivative analyzed	B. p., °C.	Halogen, % Calcd.	Found
Stearolic acid	Chloroketostearic acid	Dec.	Cl 10.66	10.68
	Bromoketostearic acid	Dec.	Br 21.20	21.07
Behenolic acid	Chloroketobehenic acid	Dec.	Cl 9.12	9.02
	Bromoketobehenic acid	Dec.	Br 18.46	18.36
Methyl octine carboxylate	Methyl dibromoketononoate	169 (14 mm.)	Br 46.49	46.31
Ethyl phenylpropiolate	Ethyl benzoyldibromoacetate	194 (15 mm.)	Br 45.72	45.92
Heptine-1	Tribromomethyl n-amyl ketone	120 (0.5 mm.)	Br 68.36	68.4
Octine-1	Tribromomethyl n-hexyl ketone	137 (0.5 mm.)	Br 65.74	65.8
Phenylacetylene	Very slight action at low temperatures			
Phenylpropiolic acid	ω-Tribromo-acetophenone	174 (14 mm.)	Br 67.22	67.0
10,11-Undecinoic acid	Trichloroketo-undecoic acid	Dec.	Cl 35.06	34.8

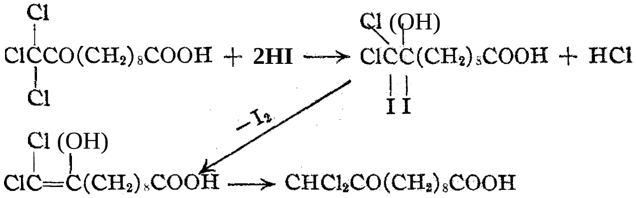
Characteristics of the Halogen Derivatives.—9-Chloro-10-ketostearic acid and the corresponding bromo acid were obtained as viscous oils which were converted into non-crystalline resinous masses by cooling with a mixture of solid carbon dioxide and ether. The sodium, potassium and lithium salts were soft and soapy. The calcium, barium and lead salts were cheese-like solids. The ethyl and methyl esters were oils which could not be distilled under a pressure of 2 mm. Both the chloro and the bromo acids were reduced to 10-ketostearic acid melting at 76° by refluxing on a water-bath with aqueous alcoholic hydriodic acid under the following conditions. 2 g. of the halogen acid was dissolved in 50 cc. of absolute alcohol and to the solution were added 5 g. of potassium iodide in 50 cc. of water and 5 cc. of concd. hydrochloric acid. The mixture was heated on a boiling water-bath under reflux for fifteen minutes and a titration made with *N*/10 thiosulfate until only a faint yellow coloration remained. The flask was again heated, thiosulfate being added at intervals of five minutes to remove free iodine. The heating was continued until only a faint coloration appeared during ten minutes. Water was added and the precipitate filtered off and recrystallized from light petroleum. The ketonic acid thus obtained was identified after establishing absence of halogen by its melting point and its unchanged melting point when mixed with the ketonic acid derived from the corresponding mercury compound by decomposition with hydrochloric acid.

13-Chloro-14-ketobehenic acid and the corresponding bromo acid were also obtained as viscous oils showing the same general characteristics as the stearic derivatives. Reduction with hydriodic acid gave 14-ketobehenic acid melting at 83–84°.

The mercury derivative of 10,11-undecinoic acid gave with chlorine the trichloro ketonic acid $Cl_3CCO(CH_2)_8COOH$ in quantitative yield. The acid and its methyl and ethyl esters were viscous oils which could not be distilled under a pressure of 2 mm.

They showed no tendency to hydrate. The acid decomposed when warmed with a 20% solution of caustic soda to yield chloroform and sodium sebacate. After one hour's reduction with aqueous alcoholic hydriodic acid under the conditions already described the acid gave an iodine-free oil containing 30.8% of chlorine. After twenty-two hours, during which liberated iodine was removed by addition of thiosulfate at intervals, an oil containing 24.2% of chlorine was obtained. Iodine was absent. Dichloro-keto-undecoic acid contains 26.26% of chlorine.

The removal of chlorine during this reaction can be accounted for by the simultaneous replacement of chlorine by iodine and the addition of hydrogen iodide to the carbonyl group.



$$\mathrm{Cl\overset{Cl}{\underset{Cl}{C}}CO(CH_2)_8COOH + 2HI \longrightarrow Cl\overset{Cl}{\underset{I}{C}}\overset{(OH)}{\underset{I}{C}}(CH_2)_8COOH + HCl}$$

$$\mathrm{Cl\overset{Cl}{C}{=}\overset{(OH)}{C}(CH_2)_8COOH \longrightarrow CHCl_2CO(CH_2)_8COOH}$$

$$\xrightarrow{-I_2}$$

The analyses recorded in this communication were effected by the methods of H. ter Meulen.

Summary

1. Mercury derivatives prepared by the action of mercuric acetate upon acetylenic compounds have been utilized for the synthesis of halogenated ketones, ketonic acids and esters.
2. Where the acetylenic compounds contain no labile acetylenic hydrogen atom, the mercury derivatives have been shown to be unsaturated and to contain the grouping $—C(OHgOOCCH_3)=C(HgOOCCH_3)—$.
3. Where the acetylenic compound contains labile acetylenic hydrogen, substitution of this hydrogen atom takes place and, while no evidence of unsaturation has been obtained, the properties of the mercury compounds can be accounted for by assuming the presence of the unsaturated grouping $—C(OHgOOCCH_3)=C(HgOOCCH_3)_2$.

LONDON, ENGLAND

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

THE REACTION BETWEEN TRIPHENYLMETHYL, MAGNESIUM AND A SMALL AMOUNT OF MAGNESIUM HALIDE. THE COMPOSITION OF THE GRIGNARD REAGENT

BY W. E. BACHMANN

RECEIVED JULY 7, 1930 PUBLISHED NOVEMBER 5, 1930

In studying the action of a mixture of magnesium and magnesium halide on ketones, 1,2-diketones and on aromatic acids,[1] it was observed that a molecule of magnesium halide was split off from the halogen-magnesium compounds initially formed in the reaction. In virtue of this regeneration of magnesium halide, a small amount of halide in the mixture could suffice for complete reaction of a large amount of the ketones or acids, provided the mixture was heated.

It has now been found that a Grignard reagent may be made to undergo a similar loss of magnesium halide

$$2(C_6H_5)_3CMgX \rightleftarrows (C_6H_5)_3CMgC(C_6H_5)_3 + MgX_2 \qquad (1)$$

Recently[2] it was shown that triphenylmethylmagnesium bromide, and the iodide, can be prepared in excellent yields from triphenylmethyl and a mixture of magnesium and magnesium halide, according to the following formulation

$$2(C_6H_5)_3C + Mg + MgX_2 \longrightarrow 2(C_6H_5)_3CMgX \qquad (2)$$

It is now found that a small amount of magnesium halide suffices for complete conversion of triphenylmethyl to its magnesium derivatives. To be sure, the reaction is slower than is the case when a large amount of halide is present, but nevertheless it is complete. Either magnesium halide, as such, or a small amount of triphenylbromomethane may be added to the triphenylmethyl and magnesium; in the latter case, the carbinol bromide is first of all changed to the radical and magnesium bromide.[2] Since the radical does not react with metallic magnesium without halide present, the magnesium halide must be continuously reproduced according to Equation 1, being made available for further reaction. At the end of the reaction there exists an equilibrium mixture of triphenylmethylmagnesium halide, magnesium triphenylmethyl and magnesium halide.

It is considered that a similar equilibrium mixture may exist in the case of this and all other Grignard reagents even when the amount of metal halide is equivalent to a full mole, as is the case with such reagents prepared from the alkyl halides. Schlenk and Schlenk, Jr.,[3] employing a different method, came to a similar conclusion. Gilman and co-workers[4] consider

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[1] Gomberg and Bachmann, THIS JOURNAL, 49,247,2584 (1927); 50,2762 (1928).

[2] Gomberg and Bachmann, *ibid.*, 52, 2455 (1930).

[3] Schlenk and Schlenk, Jr., Ber., 62, 920 (1929).

[4] Gilman and Fothergill, THIS JOURNAL, 51, 3149 (1929); Gilman and Brown, *Rec. trav. chim.*, 48, 1133 (1929).

that there is little or no $R_2Mg{\cdot}MgI_2$ in the Grignard reagent under ordinary conditions in ether solution but that the amount varies markedly with the nature of the solvent, reactant and temperature.

Experimental

Triphenylmethyl + Mg.—A mixture of 9.8 g. of triphenylmethyl and 0.62 g. of magnesium ribbon in 120 cc. of ether–benzene (1:2) was heated for forty-eight hours in an atmosphere of nitrogen. At the end of this time no weighable amount of magnesium had reacted. In another experiment no magnesium was dissolved after one hundred hours, and the triphenylmethyl used was recovered unchanged.

Triphenylmethyl + Mg + MgI_2 (42%).—Twelve grams of triphenylmethyl, 3 g. of magnesium iodide and 0.77 g. of magnesium ribbon were heated in an atmosphere of nitrogen in a mixture of 40 cc. of ether and 70 cc. of benzene. After twenty hours, the clear solution was filtered from excess of magnesium and hydrolyzed. The magnesium loss was 0.59 g.; this represents 97% of the calculated value. The magnesium hydroxide produced on hydrolysis required 46.05 cc. of N acid for neutralization; theoretical value on basis of triphenylmethyl, 50.0 cc. From the ether–benzene solution there was obtained 11 g. (92%) of triphenylmethane.

Similar results were obtained when magnesium bromide was used in place of the iodide, even when the amount of halide corresponded to only 0.05 mole for a mole of triphenylmethyl.

Triphenylmethyl (0.9 mole) + Triphenylbromomethane (0.1 mole) + Mg.—A mixture of 13.4 g. of triphenylmethyl and 1.98 g. of triphenylbromomethane was heated with 1.19 g. of magnesium ribbon in 200 cc. of ether–benzene (2:3). The reaction started immediately. After three days the solution was filtered; loss in magnesium, 0.83 g.; theoretical value, 0.82. Dry carbon dioxide was passed into the solution for six hours. Hydrolysis yielded 8.5 g. of triphenylacetic acid or 50% of the calculated amount. From this single experiment, it would appear that the reaction between magnesium triphenylmethyl and carbon dioxide is considerably slower than carbonation of triphenylmethylmagnesium bromide. Gilman and Brown[6] report that phenylmagnesium bromide reacts with n-valeronitrile more readily than does an equivalent solution of magnesium diphenyl.

In another experiment in which 13.4 g. of triphenylmethyl and 1.80 g. of triphenylbromomethane were allowed to react with magnesium, 0.80 g. of metal was dissolved; calculated, 0.80. Hydrolysis gave 11.3 g. of triphenylmethane; calculated, 14.8.

Summary

A small amount of magnesium iodide (or bromide) can suffice to convert triphenylmethyl and magnesium to the magnesium derivatives of triphenylmethyl. The reaction takes place in two steps: (a) $2(C_6H_5)_3C + Mg + MgX_2 = 2(C_6H_5)_3CMgX$; (b) $2(C_6H_5)_3CMgX \rightleftarrows MgX_2 + (C_6H_5)_3CMgC(C_6H_5)_3$. The latter step makes the MgX_2 available for continuous reaction.

ANN ARBOR, MICHIGAN

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[5] Gilman and Brown, THIS JOURNAL, 52, 1183 (1930).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO BORON. II. ACTION OF LITHIUM ON ETHYLAMMINO BORON TRIFLUORIDE

BY CHARLES A. KRAUS AND EARL H. BROWN

RECEIVED JULY 10, 1930 PUBLISHED NOVEMBER 5, 1930

As was stated in a preceding paper,[1] ammino boron trifluoride is appreciably ammonolyzed when dissolved in liquid ammonia. This is conclusively shown by the fact that when sodium is added to a solution of the trifluoride in liquid ammonia, hydrogen is evolved. It was at first thought that ethylammino boron trifluoride might dissolve in ethylamine without aminolysis. However, on adding lithium to a solution of this compound in ethylamine, three atoms of hydrogen were evolved per mole of boron trifluoride, thus showing that aminolysis went to completion.

The reaction between lithium and boron trifluoride in ethylamine may be expressed by the equation

$$BF_3 + 3C_2H_5NH_2 + 3Li = B(C_2H_5NH)_3 + 3LiF + 3/2H_2$$

Experiment has shown that the reaction proceeds practically quantitatively. The various products of the reaction have been isolated and identified.

Preparation of Tertiary Boron Ethylimine.—On adding lithium to an ethylamine solution of ethylammino boron trifluoride, hydrogen is evolved and a precipitate, consisting of lithium fluoride, is formed. This reaction is due to aminolysis of the boron trifluoride, the resulting ethyl ammonium fluoride reacting with lithium to form lithium fluoride and hydrogen. The reaction proceeds until all the fluorine atoms have been aminolyzed.

Four reactions were carried out for the purpose of determining the nature of the various reaction products. The apparatus employed was substantially as is shown in Fig. 1. The reactions were carried out in a weighed tube A. A known quantity of ethylammino boron fluoride was introduced into the bottom of the reaction tube and a weighed quantity of lithium into the introduction tube B. The reaction tube was attached to the system at T by means of de Khotinsky cement. After exhausting the apparatus, a bath of ammonia was placed around the auxiliary chamber M, into which a quantity of lithium had previously been introduced, and, by opening the valve O of the cylinder L, containing ethylamine, the desired quantity of solvent was condensed in M. After closing stopcock K, the bath surrounding M was removed and placed around the reaction tube A. Stopcocks C, D and H were opened, allowing the solvent evaporating in M to condense in the reaction tube. When condensation was completed, any hydrogen present was removed with a pump and the lithium in the addition tube B was introduced as needed by turning this tube through a suitable angle about its axis. In the meantime, the stirrer Z, suspended from a spring Y, was set in motion by an intermittent current passing through the solenoid X. Lithium was added slowly, piece by piece, the evolved hydrogen passing through stopcocks C, D and F and through a sul-

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[1] Kraus and Brown, THIS JOURNAL, 51, 2690 (1929).

furic acid trap W into the chambers V and U containing sulfuric acid and phosphorus pentoxide, respectively. The acid and oxide served to remove ethylamine carried over with the hydrogen.

The addition of lithium was continued until the solution remained permanently blue. All the hydrogen was carried over into the drying tubes by the amine vapor.

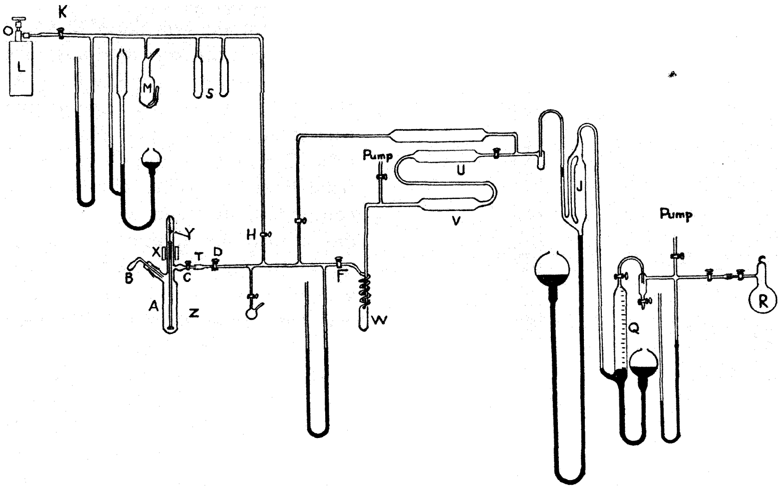

Fig. 1.—Apparatus used in aminolysis of boron trifluoride.

After standing, it was removed by means of a Topler pump, J, and transferred into a graduated buret Q. After determining the volume of the hydrogen, it was introduced into a bulb R of known volume and its density determined from the weight and pressure of the gas.

The excess solvent was distilled from the reaction tube into the recovery tubes, S, which were then sealed off from the system. Dry nitrogen was introduced into the reaction tube, the addition tube B was removed and the amount of lithium remaining, determined. The reaction tube A was then pumped to constant weight.

On weighing, it was found that the weight of the contents was less than that of the materials used. This led to the inference that one of the products of the reaction was a more or less volatile liquid or solid.

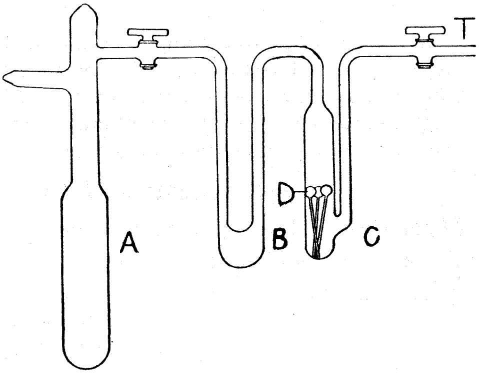

Fig. 2.—Apparatus used in preparing boron triethylimine.

Accordingly, in a third experiment, a two-legged reaction tube was used in place of that illustrated in Fig. 1. Before distilling off the amine at the end of the reaction, the tube was detached from the system, the precipitate was allowed to settle and the clear liquid decanted into the second limb of the tube. The solvent was then distilled back into the first leg for the purpose of washing the solid residue. This process was repeated nine times. The tube was then again attached to the system and the excess amine recovered. It was found that a quantity of liquid remained in the second limb of the reaction tube which was much less volatile than ethylamine. The two limbs of the reaction tube were sealed and separated from each other, and the limb A containing the liquid product was attached to two U-tubes, B and C, as shown in Fig. 2. The tube T was attached to T of the apparatus as shown in Fig. 1. The apparatus was exhausted through T while a bath of liquid ammonia was placed around tube B. Under a pressure of about 0.1 mm.. the liquid distilled rapidly from A into the cooled tube The ammonia bath was then removed and placed around tube C and the liquid was redistilled from B to C. When this process was completed, nitrogen was slowly introduced into the apparatus. forcing the liquid through the capillaries into the previously weighed bulbs D. Tube C was then opened, the bulbs were removed and the capillaries sealed and weighed The solid residue left in the first limb of the original two-legged reaction tube was treated with sulfuric acid in a platinum crucible and the weight of lithium determined as lithium sulfate.

A fourth reaction was carried out with a tube of the form shown in Fig. 3. Tube A' was attached, by means of T to tube T of Fig. 1 in place of the reaction tube A. The reaction was carried out as already described and. when completed. stopcock D was closed and tube X was attached to a pump. On placing a liquid ammonia bath around tube B (containing the weighed bulbs) and exhausting the system through *C*, the volatile product distilled rapidly from the reaction tube A' into B. This liquid was then forced through the capillaries into the bulbs under a pressure of nitrogen. The known samples in the bulbs were employed for analyses and molecular weight determinations.

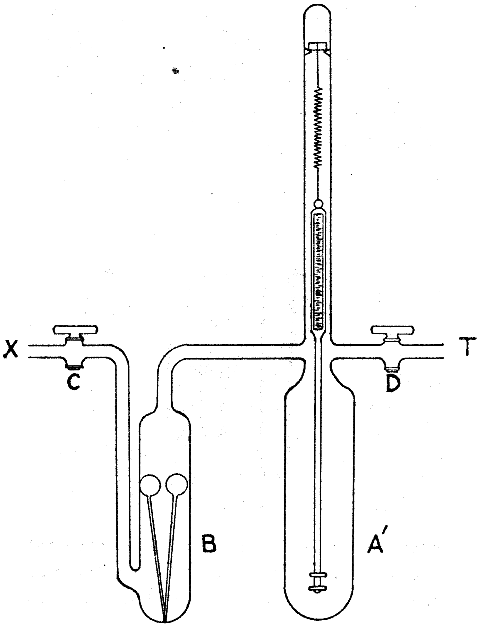

Fig. 3.—Improved apparatus for Preparing boron triethylimine.

Determination of Products of Reaction

Hydrogen.—The relation between the volume of hydrogen collected and the weights of material used is summarized in the following table for Expts. 1, 2 and 3.

TABLE I

DATA RELATING TO HYDROGEN EVOLVED

Expt. no.	Mole of BF_3	Mole Li	H_2, cc.	Atoms H_2
1	0.0095	0.037	266	0.0238
2	.00681	.0217	240	.0214
3	.00626	.0187	197.2	.0176

The density of the gas evolved in Reaction 1, was 3.36, which clearly indicates that it consisted essentially of hydrogen. As is shown by the figures in the last column, the volume of hydrogen collected in Expts. 2 and **3** was approximately three atoms per mole of boron trifluoride,

The Insoluble Solid Product of Aminolysis.—The solid product of the reaction, which was insoluble in ethylamine, was assumed to be lithium fluoride. After washing with ethylamine, various samples were analyzed for lithium and fluorine without further purification.

Anal. Lithium subs., 0.0621, 0.1898, 0.2413: Li_2SO_4, 0.1206, 0.3882, 0.4965. Calcd. for LiF: Li, 26.75. Found: Li, 24.51, 25.82, 25.87.

The solid was also analyzed for fluorine by the lead chlorofluoride method.

Anal. Subs., 0.0322: PbClF, 0.3119. Calcd. for LiF: F, 73.4. Found: F, 70.32.

The results show that the insoluble product of reduction was slightly impure lithium fluoride.

Analysis of Liquid Product $B(C_2H_5NH)_3$.—Samples of the liquid product, prepared as described above, were analyzed for nitrogen by hydrolyzing the material, distilling the ethylamine with water vapor and titrating the distillate with hydrochloric acid of known concentration.

Anal. $B(C_2H_5NH)_3$ subs., 0.0777, 0.0712: cc. of 0.1083 *N* HCl, 15.11, 13.78. Calcd. for $B(C_2H_5NH)_3$: N, 29.30. Found: N, 29.20, 29.36.

A quantity of the material was hydrolyzed by means of a small quantity of water vapor and the amine resulting was collected and its vapor density determined. The vapor density corresponded to a molecular weight of 44.8, as against 45.1 for ethylamine.

Analyses for boron were carried out by the titration method, as described in the preceding paper. In a number of instances the ethylamine was boiled off from an alkaline solution, while in others, the amine was first titrated with 0.1 *N* HCl. Samples of material from which the amine had been removed by the boiling of an alkaline solution yielded, in three determinations, 8.11, 8.27 and 8.16% of boron. In another series of determinations, in which the amine was neutralized with 0.1 N HCl, there were obtained the following values: 8.00, 7.96, 8.02 and 7.96% of boron. The boron content of $B(C_2H_5NH)_3$ is 7.67%. The value found for boron was slightly high. This discrepancy was due to inadequacy of the analytical method rather than to lack of purity of the compound.

Properties.—The properties of tertiary boron ethylimine, which is an ammono boron ethyl ester, were not extensively studied. It is fairly volatile at ordinary temperatures and, except for its sensitiveness to moisture, it is quite stable. It is readily soluble in ethylamine.

Summary

Ethylammino boron trifluoride is aminolyzed when dissolved in ethylamine. When a solution of this compound is treated with three atoms of metallic lithium, boron triethylimine, $B(C_2H_5NH)_3$, is formed. This ammono boron ethyl ester is a liquid readily soluble in ethylamine, ap-

preciably volatile at ordinary temperatures and readily hydrolyzable by water vapor.

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

COBALT COMPLEXES OF THIOGLYCOLIC ACID

BY LEONOR MICHAELIS AND MAXWELL P. SCHUBERT

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For reasons understandable from some preceding papers,[1] it seemed important to enhance our knowledge of metal complexes of sulfhydril compounds which also contain a carboxyl group. Though the behavior of various representatives of this group toward cobalt has some common aspects, there are individual differences. This paper is restricted to the simplest of these compounds, thioglycolic acid.

Compounds of cobalt and thioglycolic acid have been described by Rosenheim and Davidsohn.[2] Attempts to repeat their work did not yield readily crystallizable compounds and furthermore these authors were not aware of the fact that the formation of their brown compounds requires free oxygen and does not take place in the absence of air.

Another brief notice is given by Myers[3] but he evidently did not obtain a pure compound and was also unaware of the oxidation which takes place in its formation. Much more nearly related to the compounds described in this paper is Cremer's[4] observation of a complex established with cysteine and cobalt in the absence of air and in the presence of carbon monoxide. This complex, according to Cremer, contains two molecules of cysteine and one molecule of carbon monoxide for each atom of cobalt. The color of this complex is olive-green, more intense than the color of the cobaltous complex of cysteine without carbon monoxide. This author does not mention the fact that this cobalto complex in contact with air undergoes a considerable change and intensification of color, a fact which will be the starting point for our investigation. Cremer also describes an analogous complex of ferrous iron. One atom of iron combines with two molecules of cysteine and two molecules of carbon monoxide, so differing from the cobalt complex. This ferrous complex is highly optically active, is orange-yellow in color, and reversibly dissociates the carbon monoxide on being illuminated.

Closely related to the present work is the attempt of Cannan and Rich-

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[1] L. Michaelis and E. S. Guzman Barron, J. *Biol. Chem.*, 83, 191 (1929); L. Michaelis, *ibid.*, *84*, *777* (1929).

[2] A. Rosenheim and J. Davidsohn, Z. *anorg. Chem.*, *41*, 231 (1904).

[3] C. N. Myers, J. *Lab. Clin. Med.*, 6, 359 (1921).

[4] W. Cremer, *Biochem. Z.*, 206, 228 (1929).

ardson[5] to establish by indirect physico-chemical analysis the composition of iron thiogylcolic acid complexes. Their conclusions, however, are quite different from what will be suggested here.

Yet among the innumerable papers on cobalt complexes by such authors as Werner, Pfeiffer, Jörgensen, Weinland, Tchugaeff, Ley and others, there is not a single one concerned with compounds such as cysteine or thioglycolic acid which has in addition to an SH group some other group capable either of direct salt or complex formation so that the whole molecule would give an inner complex in the sense of Ley.[6] This is the more remarkable as many other sulfur compounds have turned out to form quite stable complexes with cobalt; even in compounds in which the sulfur seems quite saturated, such as the thioethers and disulfides, there seems to be a strong affinity between sulfur and cobalt.

When a cobalt salt is mixed with a buffer around *P*H 6–10 (phosphate, carbonate, veronal) a pink precipitate arises which is perfectly stable in air and shows no trace of any oxygen consumption when observed in a microrespiration apparatus. In the same way, the soluble slightly pink cobalt complex of pyrophosphate is not oxidized by air, in contrast to the analogous ferro complex.

When the mixture of cobalt salt and phosphate buffer, containing the slightly pink precipitate, is mixed with thioglycolic acid under such conditions that the reaction never becomes acid, the precipitate is dissolved and the color rapidly becomes brown. Under favorable conditions one may see an intermediate state of deep blue-green color. This intermediate state, difficult to observe in air, is the permanent state in absence of air. On mixing the components under completely deaerated condition in a stream of nitrogen, the green color arises and is stable. The green color may be intense at high concentration but is by no means comparable in color intensity to the brown color established in air. Instead of oxygen, ferricyanide, or a dyestuff such as indophenol, methylene blue, or even indigo disulfonate can be used as oxidant with equal effect, the dye being reduced instantaneously. The green cobalt complex is so sensitive to air that we have not attempted as yet to prepare it in pure condition. The only statement one may make is that in absence of air approximately two molecules of thioglycolic acid are necessary to dissolve one molecule of cobalt present in the form of the phosphate precipitate.

When this mixture is exposed to the air it rapidly consumes oxygen, simultaneously turning brown. To get an idea of the oxidation level of this brown complex a study was made of the amount of oxygen taken up in its formation. This study has shown that there is more than one step to the oxidation process and that by adjusting the conditions these steps

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[5] R. K. Cannan and G. M. Richardson, *Biochem. J.*, 23, 1242 (1929).

[6] H. Ley, *Z. Electrochem.*, 10, 954 (1904).

can be quite sharply distinguished. It is particularly necessary to avoid too alkaline a reaction.

The oxygen uptake was measured in a 500-cc. Erlenmeyer flask with a one-holed rubber stopper leading to a calibrated air reservoir with a manometer attachment so that the whole system could be held at atmospheric pressure. In the flask two test-tubes were placed, one with thioglycolic acid and one with alkali, while in the bottom of the flask itself was placed the cobalt salt with some primary phosphate. The whole was sealed with paraffin and after standing for at least an hour in a constant temperature room at 30° and under slight pressure to make sure there were no leaks, the flask was tipped to allow the contents of the test-tubes to mix with those of the flask and then the decrease in volume of the gas in the system was read off at successive time intervals, the flask being shaken all the time.

Under these conditions and with the amounts of material noted in the table there was observed for the first thirty minutes a rapid oxygen uptake which then dropped off quite suddenly, falling to a rate which was about one-twentieth to one-hundredth of the average rate during the first thirty minutes. After an hour the oxygen uptake had dropped to a rate of the order of 1% or less of the rate during the first thirty minutes and continued for days without reaching a definite end. The amount of oxygen taken up during this first thirty-minute interval, which quite evidently corresponds to a distinct step of oxidation, is one-eighth mole of oxygen per mole of thioglycolic acid used, provided the molecular ratio of thioglycolic acid to cobalt is not greater than two to one and provided the mixture is not too alkaline. These are the conditions under which the crystalline complexes were made and frequently isolated within an hour with yields of over 70%. If the thioglycolic acid be in excess with respect to cobalt beyond the ratio noted above, then the oxygen uptake also increases somewhat, the rate depending on the alkalinity of the solution, for the excess thioglycolic acid is oxidized by oxygen to dithiodiglycolic acid. Under these conditions it is sometimes difficult to isolate the crystalline products which are our present concern, but even under these conditions there is an approximate step in the oxidation which calculated now to the cobalt amounts to one-fourth mole of oxygen per atom of cobalt. Also, if the mixture is made too alkaline

TABLE I

OXYGEN CONSUMPTION IN MIXTURES OF COBALT CHLORIDE AND THIOGLYCOLIC ACID

The column headed "calcd. O_2 consump." is the theoretical oxygen consumption calculated as one-fourth mole of oxygen per atom of cobalt if thioglycolic is in excess to cobalt over 2 to 1. If the ratio of thioglycolic acid to cobalt is less, then one-eighth mole of oxygen per mole of thioglycolic acid is taken as the theoretical value.

Expts. 2 and 7, oxygen consumption under conditions for making complexes described; Expts. 1 and 9, oxygen consumption with excess cobalt; Expts. 3, 6 and 8 increased oxygen consumption with excess alkali; Expts. 4 and 5, increased oxygen consumption with excess thioglycolic acid.

	Composition of mixture, millimoles Volume of the whole 30–40 cc.					Observed O_2 consump., mmols.			
Expt.	Thiogly. acid	Co	KOH	KH_2PO_4	Calcd. O_2 consump., mmols.	30 min.	3 hrs.	20 hrs.	% Excess of O_2 consumed in first hour over calcd.
1	6.5	6.5	21	4.5	0.81	0.93	1.11	1.54	26
2	14.4	6.5	23	4.5	1.62	1.47	2.01	2.37	7
3	14.4	6.5	52	4.5	1.62	1.98	2.98	3.99	53
4	10.3	2.5	15	9	0.63	0.67	0.90	1.23	24
5	10.3	3.4	19	9	.85	.98	1.13	1.44	23
6	10.3	3.4	37	9	.85	1.42	1.59	2.11	76
7	10.3	5.0	22	9	1.25	1.21	1.44	1.62	6
8	10.3	5.0	45	9	1.25	1.65	1.80	3.32	38
9	10.3	10.0	37	9	1.29	1.26	1.52	1.80	8

the second slow step of oxidation seems to be speeded up so that the two steps are not as sharply separated and the total oxygen uptake is increased This is probably due to a slow oxidation of the sulfur in the complex.

We were interested in the problem whether the consumed oxygen might be completely reduced or in part stay in the form of hydrogen peroxide. The only test for hydrogen peroxide in a solution of such a deep color is the test with chromic acid and extraction of the blue chrom-peroxide by ether (or better still ethyl acetate). When there is an excess of thioglycolic acid, with respect to cobalt (referred to the normal ratio 2 : 1), there is no hope of detecting hydrogen peroxide because thioglycolic acid, when not combined to form the metal complex, is rapidly oxidized by hydrogen peroxide; but on working with the ratio 2 : 1, traces of peroxide could be detected in some of the experiments. It is very likely that the formation of hydrogen peroxide depends on the partial pressure of free oxygen and on the rate of stirring, as Wieland and Franke[7] have shown for the oxidation of cobalto-hexacyanide by oxygen. At any rate, even in the best case we found only a minute trace of peroxide under such conditions where in the analogous case of cobalt cyanide a very conspicuous amount of peroxide could be found, as has been shown already by Manchot and Herzog[8] and also by Wieland.

So we may state with a fair degree of accuracy that in a mixture of one atom of cobalt and two molecules of thioglycolic acid, one-fourth of a molecule of oxygen is used up with no, or no appreciable, residue of hydrogen peroxide, during the first, rapid stage of the oxidation, with which this paper is concerned, and that the compounds to be described here represent such a state of oxidation that the cobalto-thioglycolic acid complex has consumed one-fourth of a molecule of oxygen for each atom of cobalt. This is no more oxygen than would be necessary to oxidize the cobaltous state to the cobaltic, without further oxidation of the sulfur groups. It should be emphasized that this stage of oxidation is not the highest obtainable but it is the first product of oxidation which is stable enough to isolate in pure condition. Only with this stage of oxidation is the present paper concerned.

The Preparation of the Complexes.—The simplest of these cobalt-thioglycolic acid complexes to prepare is the potassium salt. 10 cc. of thioglycolic acid (140 millimoles) is dissolved in 15 cc. of water and then 20 cc. of 7.5 *M* potassium hydroxide is added. This potassium thioglycolate solution is then poured into a mixture of 130 cc. of cobalt chloride (0.5 M), 50 cc. of potassium dihydrogen phosphate (0.9 M) and 19 cc. of potassium hydroxide (7.5 M) with rapid stirring. The mixture immediately turns a deep red-brown. On examination under a microscope the solution now appears practically clear. The mixture should be shaken or stirred in contact with the air or have air bubbled through it for an hour. If necessary it is filtered. The solution is

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[7] H. Wieland and W. Franke, Ann., 473, 289 (1929).

[8] W. Manchot and J. Herzog, Ber., 33, 1742 (1900).

evaporated either *in vacuo* or over steam to about one-third its volume. After cooling in the ice box for an hour or two, the crop of crystals is filtered off on a Büchner funnel and sucked as dry as possible. This product dissolves readily and completely in water, giving an intensely colored red-brown solution. It is dissolved in about 125 cc. of water and 95% alcohol is added slowly and with stirring until about 125 cc. has been added. An amorphous precipitate immediately appears which rapidly becomes crystalline. The crystals observed under low magnification are thin rectangular plates pointed at the ends. After standing for a few hours they can be filtered on a Büchner and washed first with 50% alcohol, then with 95% alcohol. The yield after drying for a day or two in the air is over 16.5 g. or over 75% calculated on the basis of the composition found by analysis. After drying by exposure to the air for a few days the following analytical results were obtained.

Anal. Calcd. for $[Co(SCH_2COO)_2KH]_2O{\cdot}5H_2O$: K, 11.76; S, 19.28; Co, 17.74; H_2O, 13.55. Found: K, 11.55; S, 19.31; Co, 17.83; H_2O, 13.07.

The potassium salt which has just been described is the best starting point for the preparation of the rest of the compounds studied here. To prepare the barium salt 3 g. of the recrystallized potassium salt is dissolved in 150 cc. of water and an aqueous barium chloride solution is added. An amorphous precipitate forms immediately, which begins to crystallize only after standing for about an hour. The crystallization is watched under a microscope and may take from one to four or five days for completion. Then the crystals are filtered off and washed several times with water and finally with 95% alcohol. The yield of the air-dried product is 3.2 g. This salt is quite insoluble in cold or hot water and dissolves only partially on addition of concentrated hydrochloric acid. The following analytical results are on the air-dried product.

Anal. Calcd. for $Ba[Co(SCH_2COO)_2H]_2O{\cdot}5H_2O$: Ba, 18.96; S, 17.72; Co, 16.30; H_2O, 12.45. Found: Ba, 18.87; S, 17.41; Co, 16.41; H_2O, 12.02.

Another crystalline product which appears to bc an acid potassium salt may also be obtained from the potassium salt already described. About 15 g. of the potassium salt is dissolved in 75 cc. of water, then drop by drop and with constant stirring 3.5 cc. of concentrated hydrochloric acid is added. The mixture is set on ice for about twelve hours. The solution then turns almost solid with a light brown precipitate which under the microscope appears as exceedingly fine hair-like crystals. They are difficult to filter and are best separated by centrifuging. Then they are dissolved in about 250 cc. of water. In contrast to the former potassium salt these crystals dissolve only very slowly. After solution is complete alcohol is stirred in slowly and in small portions until about 150 to 200 cc. has been added. An amorphous precipitate appears which sometimes crystallizes in an hour or two and at other times does so only after standing for a week. The crystals are filtered off, washed with 50% alcohol, then with 95% alcohol and dried by exposure to air. This air-dried product amounts to 7 g.

Anal. Calcd. for $KH[Co(SCH_2COO)_2H]_2O{\cdot}4H_2O$: K, 6.42: S, 21.07; Co, 19.37; H_2O, 11.84. Found: K, 7.17; S, 20.39; Co, 19.72; H_2O, 12.66.

The free complex acid corresponding to the compounds which have been described can be prepared from the acid potassium salt by dissolving the latter in water and adding concentrated hydrochloric acid drop by drop with steady stirring until a permanent precipitate is formed. Under the microscope the precipitate appears as very short narrow bars. These are filtered off after several hours, washed with 30% alcohol and finally with 95% alcohol. After drying in the air, these crystals were analyzed.

Anal. Calcd. for $[Co(SCH_2COOH)_2]_2O{\cdot}3.5H_2O$: S, 22.87; Co, 21.01; C, 17.10; H, 3.42; H_2O, 11.24. Found: S, 23.04; Co, 21.45; C, 16.88; H, 3.21; H_2O, 11.26.

All of these complexes are quite stable and hydrogen sulfide, potassium hydroxide and potassium ferrocyanide all fail to precipitate the cobalt. The dry crystalline compounds are quite stable and can be heated to 140° without decomposition provided they are not heated for too long a time. The aqueous solutions of these compounds are intensely reddish-brown, with no band in the visible part of the spectrum but with increasing absorption toward the violet end.

The analytical results given are in all cases the mean results of duplicate analyses run on two or three entirely independent preparations.

For the C and H determinations we are indebted to Dr. Elek.

In the case of the potassium salt and the barium salt, water was determined by heating to constant weight at 110 to 120°. In the case of the potassium salt subsequent exposure to the air brought about, in a week, a recovery of most of the lost weight. The acid potassium salt and the free acid seem to begin to decompose slowly after heating for a few days at 120°, so in these cases water was determined in a vacuum desiccator over sulfuric acid.

Discussion of the Constitution.—In setting up formulas for the compounds which have been described, the oxygen consumption studies must be considered as well as the analytical figures. All the compounds show a sulfur to cobalt ratio of 2:1 and where carbon and hydrogen have also been determined the results show that the thioglycolic acid molecule behaves as a unit in coordinating with the cobalt. Furthermore, in none of these compounds has there ever been found any negative radical other than the thioglycolate although made in the presence of chloride, phosphate or pyrophosphate. The complex nucleus of the compounds considered here, therefore, consists of two molecules of thioglycolic acid distributed around the cobalt atom. This nucleus forms the negative ion of the compounds.

The oxidation level for a unit consisting of a cobalt atom and two thioglycolate radicals is such that one electron is lost for each such unit. This could mean either that the cobalt is oxidized from a cobaltous to a cobaltic condition or that half the thioglycolic acid is oxidized to a disulfide form.

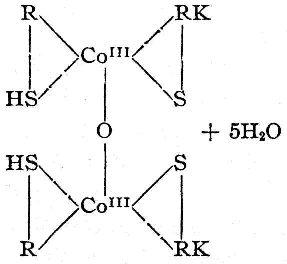
Finally, the existence of the acid potassium salt with one potassium atom to two cobalt atoms and four thioglycolate radicals suggests the possibility that these complexes may be dinuclear in structure.

To get some further evidence to show whether the compounds were mono- or dinuclear, the freezing point depressions of aqueous solutions of the potassium salt were determined. The results were: (a) 0.091° lowering of freezing point of water in a solution of 0.3884 g. of the potassium salt in 20.10 g. of water; (b) 0.147° lowering for 0.6389 g. of the potassium salt in 17.65 g. of water. This is, on the average, a freezing point depression of 0.0044' for each gram of substance dissolved in 1000 g. of water. The expected depression for a solution 1:1000 would be, assuming total dissociation of all potassium ions

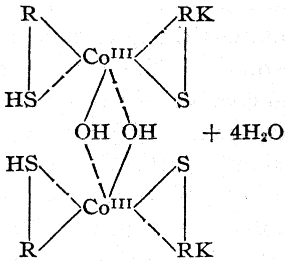
For the monomolecular formula	0.0112°
For the dimolecular formula	0.0084°

It can be seen that the monomolecular formula is not in accordance with the observed freezing point at all. The dimolecular formula is more compatible, taking into consideration that in electrolytes with polyvalent anions the assumption of 100% dissociation and the neglecting of osmotic coefficients (in the sense of Debye) are not justifiable and necessarily render the calculated depression greater than it can really be. Even a higher polymerization might be in agreement with the observed freezing point. Anyhow, this method is not very conclusive for polyvalent electrolytes and may be only utilized here to discredit a monomolecular formula.

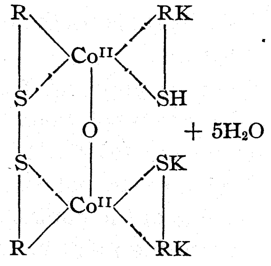
Putting all these facts together leads to the following tentative formulas in which Ia and Ib represent a cobaltic compound, IIa and IIb a cobalto-disulfide compound, both in the form of the potassium salt. The two b-formulas are analogous to what Werner designated as 01-complexes. They have the advantage that the six coordination places around the central cobalt are occupied and at the same time account for the fact that the crystals of both the free acid and the potassium salt, as well as the barium salt contain an odd number of water molecules (as reckoned for the bi-molecular formula). The odd water molecule may be the one which the two b-formulas have in the inner spheres of the cobalt atoms, and which the a-formulas do not have.



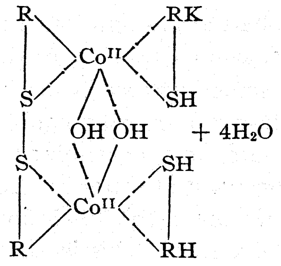
Ia



Ib



IIa



IIb

$R = SCH_2COO$

A similar formulation of some cobalt complexes which are somewhat analogous to the ones here described is given by Durrant,[9] who also at-

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[9] R. G. Durrant, *J. Chem. Soc.*, 87, 1781 (1905).

tempted to determine the oxidation level as well as the molecular weight of the compounds he describes, particularly of the oxalate compounds.

So far no isomers have been found. It may be that the residual valences between pairs of sulfur atoms, even in the saturated form as SH groups, prevent them from taking a tmns-position instead of cis, and so prevent the formation of isomers.

As we attempt to bring up various arguments for the preference of one or the other of the two possibilities I or II, the following ideas may be set forth.

Nickel sulfate (or chloride) reacts, under the same conditions as cobalt, with thioglycolic acid, giving a red color, but is the same in the absence or in the presence of oxygen. Oxygen consumption is, therefore, not involved in the establishment of this compound. This complex is, therefore, most likely analogous to the slightly green cobaltous complex which arises in the absence of oxygen. Ferrous salts, under similar conditions, and in the absence of oxygen, form a practically colorless soluble complex with thioglycolic acid, which combines avidly with oxygen and forms the red complex differing from the oxidized cobalt complex by its lability so that iron is a catalyst for the oxidation of thioglycolic acid to dithiodiglycolic acid. The behavior of the three complexes: ferrous, nickelous and cobaltous cysteine, toward oxygen is, therefore, what may be anticipated from the general properties of the metals, but scarcely from the general property of thioglycolic acid. Nickel compounds are under any conditions stable only in the nickelous state. Cobalt compounds are in certain compounds stable only in the cobaltous state (cobalt sulfate, chloride, etc.), in others they are, when produced in the cobaltous state, spontaneously and completely oxidized even by moleular oxygen to the cobaltic state and then cannot be reduced to the cobaltous state even by powerful reductants. Iron compounds can always be shifted easily from the ferric state to the ferrous and *vice* versa. From this point of view, the cobaltic formula No. 1 is preferable.

On the other hand, the high affinity of the two sulfur atoms, deprived of the H-atoms, in such a vicinity as indicated in the formula should be taken into account. This might involve a secondary change of formula I to II.

Many attempts have been made to decide between the two possible formulations, but with no decisive result as yet. One may think of a desmotropic relationship between the two formulas. This idea might account for the intense color of the complexes. Anyhow, the very fact that such a doubt is possible at all hints at the close relationship between a cobaltihydrosulfide form and a cobalto-disulfide form, and seems to be an approach toward an understanding of the metal catalysis in the oxidation of hydro: sulfides to disulfides.

Summary

Some crystalline complex compounds of cobalt and thioglycolic acid have been prepared and on the basis of chemical analysis and oxygen consumption their possible constitutions have been discussed. The bearing of these constitutions on the heavy metal catalysis of the oxidation of thiol acids has been pointed out.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO METHYL TIN DERIVATIVES. VI. THE REACTION BETWEEN CHLOROFORM AND SODIUM TRIMETHYL STANNIDE IN LIQUID AMMONIA

BY CHARLES A. KRAUS AND ARTHUR M. NEAL

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As was shown in an earlier paper[1] sodium trimethyl stannide reacts with methylene chloride in liquid ammonia with the formation of di-trimethyl stannyl methane. It might, therefore, be expected that a corresponding reaction would take place between chloroform and sodium trimethyl stannide according to the equation

$$3(CH_3)_3SnNa + CHCl_3 = [(CH_3)Sn]_3CH + 3NaCl \qquad (I)$$

Indeed, when chloroform is added to a solution of sodium trimethyl stannide in liquid ammonia, reaction takes place immediately with the formation of a white precipitate which, in part at least, is solid. On evaporation of the ammonia, an oily liquid is left behind, which might be expected to be tri-trimethyl stannyl methane. A closer investigation of this liquid, however, showed that it consisted of at least two substances and it was found necessary to examine the product at length in order to establish the nature of the substances in question. The various experiments relating to this study are described below.

Preliminary Experiments.—A quantity of sodium trimethyl stannide was treated with chloroform in liquid ammonia. When the reaction was completed, the ammonia was allowed to evaporate and the oily liquid left behind was washed several times, first with ammonia water and, finally, with distilled water. The liquid was separated from the water layer and dried by filtering through anhydrous sodium sulfate in an atmosphere of nitrogen. Samples were sealed in weighed tubes from which the air had been displaced by nitrogen.

Samples of the product were analyzed for tin by the Carius method.

Anal. Subs., 0.3403, 0.3841: SnO_2, 0.3046, 0.3433. Calcd. for $[(CH_3)_3Sn]_3CH$: Sn, 70.64. Found: Sn, 70.73, 70.40.

The molecular weight of the compound was determined by the cryoscopic method with benzene as solvent.

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[1] Kraus and Neal, THIS JOURNAL, 52, 695 (1930).

Mol. wt. Solvent, 33.25, 33.25; solute, 0.8495, 0.7541; Δt, 0.400, 0.335°; mol. wt., 319.1, 338.5. Calcd. for $[(CH_3)_3Sn]_3CH$: mol. wt., 504.1.

While the results of analysis correspond fairly well with those required for tri-trimethyl stannyl methane, the mean molecular weight of the substance in benzene is clearly incompatible with this formula. A re-examination of the product initially formed in liquid ammonia showed that it was partly liquid and partly solid at liquid ammonia temperatures and that the solid disappeared at 0°.

It was suspected that the product was a mixture, one constituent of which was trimethyl tin. The latter compound combines readily with iodine and the trimethyl tin iodide formed may be precipitated from most solvents by means of gaseous ammonia. Accordingly, known weights of the original preparation were treated with a standard solution of iodine in carbon tetrachloride. In four experiments, from 1.7 to 1.8 atoms of tin in the original mixture reacted with one atom of iodine. In other words, approximately four-sevenths of the original mixture consisted of trimethyl tin. It is difficult to account for this ratio except by assuming a loss of trimethyl tin in the process of purification. This is borne out by the variation observed in this ratio.

The solutions, after iodination, were treated with ammonia. Any trimethyl tin iodide present was precipitated and recovered. Samples of the precipitated product were analyzed for iodine and tin.

Anal. Subs., 0.2332, 0.3757: AgI, 0.1760, 0.2852. Calcd. for $(CH_3)_3SnI\cdot NH_3$: I, 41.25. Found: I, 40.79, 41.03. Subs., 0.1682: SnO_2, 0.0838. Calcd. for $(CH_3)_3SnI\cdot NH_3$: Sn, 38.59. Found: Sn, 39.24.

The analyses, as well as the properties of the compound, show clearly that trimethyl tin iodide is one of the products of iodination of the original mixture. Nearly all the iodine concerned in the reaction is converted to trimethyl tin iodide. In one experiment, 2.716 g. of iodine was required for iodination and 2.566 g. was recovered as trimethyl tin iodide.

Seemingly, one constituent of the original product of reaction between sodium trimethyl stannide and chloroform is trimethyl tin. The second constituent of this product appears to be resistant to the action of iodine and, even, as later experiments have shown, to bromine at ordinary temperatures. The original reaction proceeds smoothly and, seemingly, quantitatively, except for losses that seem to be due chiefly to trimethyl tin. We may account for the products of the reaction by assuming that tri-trimethyl stannyl methane is formed as an intermediate product according to Equation I, and that this, in turn, breaks down according to the reaction equation

$$2[(CH_3)_3Sn]_3CH = 2[(CH_3)_3Sn]_2 + (CH_3)_3SnCH{=}CHSn(CH_3)_3 \qquad \text{(II)}$$

The second constituent of this reaction, di-trimethyl stannyl ethylene, is an unsaturated aliphatic derivative and might be expected to add halogens. This, however, is not the case. Nevertheless, the experiments which we have carried out seem to indicate that this compound is, in fact, formed as one of the products of interaction between sodium trimethyl stannide and chloroform.

Properties of Di-trimethyl Stannyl Ethylene.—The second constituent of the product formed by the interaction of chloroform and sodium trimethyl stannide was isolated by evaporating the ethereal solution after removal of the trimethyl tin by means of iodine and ammonia, as described above. The last traces of ether were removed by means of a vacuum pump. The resulting product appeared to be a substantially pure compound which is quite stable and which boils at 194–195° under atmospheric pressure. It does not solidify at liquid ammonia temperatures.

The molecular weight of the compound was determined by the cryoscopic method, using benzene as solvent. The following results were obtained.

Mol. *wt.* Solvent, 35.60, 18.72, 19.49: solute, 1.7447, 0.2169, 0.9320; *At,* 0.704, 0.166, 0.692"; mol. wt., found, 348.0, 349.0, 345.6; calcd. for $[(CH_3)_3SnCH]_2$, 353.4.

The last experiment was carried out with a sample specially purified, as will be described below.

The compound was analyzed for tin by the Carius method.

Anal. Subs., 0.2521, 0.2038, 0.1952: SnO_2, 0.2153, 0.1729, 0.1665. Calcd. for $[(CH_3)_3SnCH]_2$: Sn, 67.17. Found: Sn, 67.27, 66.83, 67.19: mean, 67.10.

Carbon and hydrogen determinations were also made on the compound but it was difficult to obtain entirely satisfactory results, owing chiefly to the fact that it was very difficult to obtain an even combustion of the material.[2] The following results were obtained.

Anal. Subs., 0.2672, 0.4356, 0.1910: H_2O, 0.1444, 0.2368, 0.3901; CO_2, 0.2604, 0.3901, 0.1779. Calcd. for $[(CH_3)_3SnCH]_2$: H, 5.70; C, 27.15. Found: H, 6.05, 6.09, 6.19, mean, 6.11; C, 26.58, 24.43, 25.39, mean, 25.47.

While the results of these analyses are somewhat variable, when taken in connection with the analyses for tin and the molecular weight of the compound, there seems little doubt but that the formula assigned to it is correct. It seems strange, however, that a compound having a pair of doubly bonded carbon atoms should be so stable, generally, toward the halogens.

If di-trimethyl stannyl methane is one of the primary products of the original reaction, then, in order to account for the results obtained on iodination, it is necessary to assume that some trimethyl tin is lost prior to iodination. It seems that the difference in the tin content of a mixture corresponding to the formula $[(CH_3)_3Sn]_3CH$ and one in which three parts of the ethylene derivative are mixed with four parts of trimethyl tin, might be detected by analysis. Accordingly, careful analyses for tin were carried out by the Carius method with the following results.

Anal. Subs., 0.4761, 0.1698: SnO_2, 0.4238, 0.1511. Found: Sn, 70.12, 70.10; mean, 70.11.

For a mixture corresponding to the formula of tri-trimethyl stannyl methane, 70.64% of tin is required, while for a mixture containing three moles of the ethylene compound to four moles of trimethyl tin, $[(CH_3)_3Sn]_2$, 70.20% is required.

Bromination of $[(CH_3)_3SnCH]_2$.—Although di-trimethyl stannyl ethylene is inactive toward bromine at ordinary temperatures, bromination takes place slowly in boiling carbon tetrachloride. A known weight of the ethylene derivative was accordingly treated with bromine and, when the reaction was completed, the mixture was allowed to cool and ammonia was passed through the solution. A precipitate was formed which, on analysis, was shown to be diammino dimethyl tin dibromide, $(CH_3)_2SnBr_2 \cdot 2NH_3$. The precipitate was thrown on a filter, washed, dried and analyzed.

Anal. Subs., 0.1914, 0.3170: AgBr, 0.2128, 0.3484. Calcd. for $(CH_3)_2SnBr_2 \cdot 2NH_3$: Br, 46.66. Found: Br, 47.34, 46.78. Subs., 0.1461: SnO_2, 0.0632. Calcd. for $(CH_3)_2SnBr_2 \cdot 2NH_3$: Sn, 34.66. Found: Sn, 34.07.

The amount of tin recovered in the form of diiethyl tin dibromide was 1.1 g., while the amount of tin present in the original compound was 1.17 g. It seems that, on bromination, the following reaction occurs

$$(CH_3)_3SnCH{=}CHSn(CH_3)_3 + 4Br_2 = 2(CH_3)_2SnBr_2 + 2CH_3Br + 2C_2H_2Br_2 \quad \text{(III)}$$

Action of Sodium on Di-trimethyl Stannyl Ethylene in Liquid Ammonia.—To gain some further knowledge as to the constitution of the above compound, it was introduced

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[2] For these determinations we are indebted to Mr. E. Alison Flood of this Laboratory.

into a reaction tube and treated with metallic sodium in liquid ammonia. As reaction proceeded, gas was evolved, the solution acquired a yellow color and a fine granular precipitate was formed. This precipitate was doubtless sodium amide. The evolved gas proved to be methane. On adding ammonium bromide to the reaction products in the tube, the precipitate disappeared and a gas was evolved which proved to be hydrogen. After disappearance of the sodium amide, further addition of ammonium bromide resulted in the precipitation of an oily liquid which was highly volatile. The reactions appeared to be similar to those previously studied in the case of di-trimethyl stannyl methane.'

Weighed samples of di-trimethyl stannyl ethylene in sealed bulbs were introduced into the reaction tube, in which they were then broken. The compound in question had previously been prepared in considerable quantity and was subjected to fractional distillation under a pressure of 17 mm., under which condition it boiled at 85–86.5°. No sign of decomposition was observable. The product was analyzed for tin, the results of which analyses have already been given. The results of these reduction experiments are tabulated.

TABLE I

REDUCTION OF DI-TRIMETHYL STANNYL ETHYLENE

Compound, g.	Sodium, g.	Gas evolved, cc.	Mol. wt. evolved gas
2.5221	0.5979	133.4	16.1
2.2803	.5979	136.6	17.7

M. moles compound	M. atoms sodium	Atoms sodium per mole of compound	Mole of gas per mole of compound
7.13	26.00	3.65	0.84
6.45	26.00	4.03	.95

As may be seen from the table, approximately four atoms of sodium were required to reduce the compound completely. In general, an excess of metal was added, which excess was determined by titrating back with ammonium bromide. This method is not precise, as there is a tendency for particles of ammonium bromide to adhere in the colder portions of the reaction tube, which, in general, leads to values for the reacted sodium that are too low. The evolved gas was passed through a concentrated solution of sodium in liquid ammonia to remove volatile tin compounds. Any loss in the tin compounds leads to low values for the amount of gas evolved. In the two experiments for which the data are given, the compound was dropped slowly into a concentrated solution of sodium in liquid ammonia. Under these conditions, reaction takes place immediately and there is less chance for loss of the compound. The relative amount of gas obtained in these experiments was markedly higher than that obtained in earlier experiments, in which the metal was dropped into a solution of the compound in liquid ammonia.

Samples of gas were analyzed by the explosion method. The results of three such analyses are given below.

Assuming the gas to be methane, the following reaction occurs on explosion

$$CH_4 + 2O_2 = CO_2 + H_2O \text{ (liquid)}$$

TABLE II

ANALYSIS OF EVOLVED GAS

	Cubic centimeters		
Vol. gas taken	20.4	13.8	24.3
Vol. oxygen added	61.4	75.0	67.2
Total vol.	81.8	88.8	91.5
Vol. after explosion	41.0	62.4	42.8
Contraction of vol. on explosion	40.8	26.4	48.6
Vol. after absorbing CO_2	21.0	49.2	18.8
Vol. CO_2 absorbed	20.0	13.2	24.1

The contraction on explosion, should be equal to twice the volume of methane and the contraction of volume, on absorption of carbon dioxide, should be equal to the original volume of methane. As may be seen, the results of analyses are in excellent agreement with the reaction equation for methane. There can be no doubt, therefore, that when di-trimethyl stannyl ethylene is reduced by means of sodium in liquid ammonia, one mole of methane is evolved per mole of compound. The reaction equation may be written as follows

$$(CH_3)_3SnCH{=}CHSn(CH_3)_3 + 4Na + 2NH_3 = (CH_3)_3SnNa + CH_2{=}CHSn(CH_3)_2Na + 2NaNH_2 + CH_4 \quad (IV)$$

Actually, the reaction takes place in two stages. First, the linkage between a trimethyl tin group and an ethylenic carbon atom is broken down according to the reaction equation

$$(CH_3)_3Sn{=}CHSn(CH_3)_3 + 2Na + NH_3 = (CH_3)_3SnNa + CH_2{=}CHSn(CH_3)_3 + NaNH_2 \quad (V)$$

Trimethyl vinyl tin in turn is reduced by sodium, a methyl group being split off according to the equation

$$CH_2CH{=}Sn(CH_3)_3 + 2Na + NH_3 = CH_2{=}CHSn(CH_3)_2Na + CH_4 + NaNH_2 \quad (VI)$$

Thus, as a net result of the reaction, there is obtained an equimolar mixture of sodium trimethyl tin and sodium dimethyl vinyl tin.

Preparation of Trimethyl Vinyl Tin.—According to the above reaction equations, the liquid ammonia solution, on completion of the reaction, contains sodium trimethyl stannide and sodium dimethyl vinyl stannide. It is difficult to separate the trimethyl tin from the dimethyl vinyl derivative. The final product of the reaction, after evaporation of the ammonia, had a markedly different appearance from pure sodium trimethyl tin, The mixture seemed to be much more stable at ordinary temperatures and was of a bright yellow color.

It was thought that some information might be gained as to the existence of the vinyl compound by treating the reaction mixture with methyl iodide, which would lead to the formation of tetramethyl tin and trimethyl vinyl tin. This reaction was accordingly carried out. Since both tetramethyl tin and trimethyl vinyl tin are highly volatile compounds and in order to avoid loss, alcohol was added to the reaction products in the reaction tube and then water. The reaction tube was then removed from the ammonia bath and water was added until the tube was nearly filled. The supernatant aqueous solution was siphoned off and the light oil in the bottom was washed several times with fresh water. The bottom of the reaction tube was then cut off, traces of water were removed with filter paper, the tube was suspended in liquid ammonia to freeze the last drops of water and, while it was still cold, the liquid was transferred to a second tube through a fine capillary. In this tube the liquid was washed several times with liquid ammonia in order to remove traces of water. The tube was then sealed and evacuated. The molecular weight of the vapors of this liquid was then determined by the vapor density method. In general, the temperature of the tube containing the liquid was kept at least several degrees below room temperature. The pressure was read on a specially constructed closed-end manometer, the limbs of which had a diameter of 18 mm. The difference in level of the mercury columns was read by means of a cathetometer and the readings were reproducible within 0.05 mm. Appropriate corrections were applied for the temperature of the mercury, etc.

In a first series of measurements, the density varied from 184.7 initially to 194.2 at the end. There was a small amount of liquid left in the bottom of the tube at the end of these experiments which was much more difficultly volatile than the remainder. The more volatile constituents were accordingly condensed and a second series of density determinations was carried out. As may be seen from Table III, the molecular weight of the vapor increased continuously from 181.1 to 190.9. The molecular weight of tetramethyl tin is 178.8 and that of trimethyl vinyl tin is 190.8.

TABLE III

MEAN MOLECULAR WEIGHT OF VAPOR MIXTURES OF TETRAMETHYL TIN AND TRIMETHYL VINYL TIN

Volume of density bulb = 345.7 cc.

Vapor, g.	Pressure, cm.	Temp. of vapor, °C.	Mol. wt.
0.1351	4.028	26.1	181.1
.1298	3.862	25 9	181.3
.1756	5.188	26.5	183.0
.1895	5.599	26.8	183.1
.1487	4.385	27.1	183.8
.1295	3.805	27.0	184.3
.1475	4.314	27.0	186.0
.1372	3.988	27.4	186.1
.1380	4.014	27.5	186.5
.0873	2.488	28.4	190.9

The determinations of molecular weights by the vapor density method show clearly that the material consisted of a mixture of two substances whose molecular weights correspond closely to those of tetramethyl tin and trimethyl vinyl tin. Further work will be required in order to definitely establish the existence of trimethyl vinyl tin. The results support the experiments previously described as indicating the formation of di-trimethyl stannyl ethylene when sodium trimethyl tin reacts with chloroform.

An attempt was made to prepare di-trimethyl stannyl ethylene by the action of sodium trimethyl tin on acetylene chloride. It was found that, while reaction took place readily, the tin derivative was all converted to trimethyl tin.

Action of Carbon Tetrachloride on Sodium Trimethyl Tin and Sodium Triethyl Tin.—Carbon tetrachloride reacts readily with sodium trimethyl tin, the chief product of the reaction being trimethyl tin or hexamethyl stanno-ethane. The trimethyl tin separates as the reaction proceeds. A sample of the product gave a molecular weight of 319.5 in benzene, which is in good agreement with 327.4, the molecular weight of the stanno-ethane. On analysis, it was shown that the compound contained 72.65% of tin, while that required for hexamethyl stanno-ethane is 72.48.

All the tin originally present in the reacting materials was recovered as stanno-ethane. In one experiment 0.155 cc. of carbon tetrachloride was allowed to react with sufficient sodium trimethyl tin to complete the reaction. The carbon tetrachloride used was equivalent to 0.2208 g. of chlorine. The chlorine was recovered in the form of silver chloride at the end of the reaction. The silver chloride weighed 0.8706 g., which is equivalent to 0.2154 g. of chlorine. This shows that the chlorine was completely removed from the carbon tetrachloride. What happens to the carbon atom of the tetrachloride has not, as yet, been determined. It probably reacts with the solvent.

Sodium triethyl tin reacts with carbon tetrachloride in the same way as does sodium trimethyl tin. The chief product of the reaction is hexaethyl stanno-ethane. The molecular weight (in benzene) of the product obtained was 413.1, as against 411.4 required for the stanno-ethane.

Summary

The reaction between chloroform and sodium trimethyl stannide in liquid ammonia has been investigated. A tertiary substitution product is not formed but there is produced a mixture of trimethyl tin and di-trimethyl stannyl ethylene. The latter compound is a liquid boiling at 194–195° and having a normal molecular weight in benzene. The halogens do not add readily to the ethylenic group. At higher temperatures bromine reacts with the formation of dimethyl tin dibromide.

On reducing di-trimethyl stannyl ethylene with sodium in liquid ammonia

there is formed an equimolar mixture of sodium trimethyl stannide and sodium dimethyl vinyl stannide, along with methane and sodium amide. On adding methyl iodide to this mixture there is produced a mixture of tetramethyl tin and trimethyl vinyl tin. Trimethyl vinyl tin has not as yet been obtained in the pure state.

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

THE FRIEDEL AND CRAFTS REACTION WITH 8-HYDROXYQUINOLINE

BY KONOMU MATSUMURA

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On adopting the method of Behn and Rosenmund,[1] the Friedel and Crafts reaction was found to be applicable to 8-hydroxyquinoline and this paper deals with the preparation of 5-acetyl-, 5-benzoyl- and 5-chloro-acetyl-8-hydroxyquinoline. That the acyl radicals which have been introduced occupied position 5 could be ascertained by converting these compounds into the known substances either by a Beckmann rearrangement of their oximes or by reduction, respectively.

Experimental

5-Acetyl-8-hydroxyquinoline.—On introducing acetyl chloride (25 g.) into the solution of 8-hydroxyquinoline (43.5 g.) in nitrobenzene (400 g.), yellow precipitates separated. On the addition of aluminum chloride to it 100 g. at a time under shaking, the precipitates disappeared and a clear solution resulted. It was kept at 70° for twelve hours in a flask fitted with a calcium chloride tube. On cooling, some crushed ice and 100 cc. of hydrochloric acid (10%) were added to it and the separated nitrobenzene was driven off with steam. On standing overnight, the separated hydrochloride of 5-acetyl-8-hydroxyquinoline was filtered. It was dissolved in water and on the addition of sodium acetate to it, the free base separated out. It was recrystallized from hot water; yield, 25.5 g. (45% of the theoretical) after recrystallization.

It forms in colorless hair-like needles from hot water, m. p. 112–112.5°. It is fairly easily soluble in the usual organic solvents, dilute mineral acid or alkali. It gives a green color with ferric chloride and a deep red color with diazotized sulfanilic acid and alkali.

Anal. Subs., 5.043 mg.: CO_2, 13.029; H_2O, 2 111. Subs., 6.715: N_2, 0.421 (15°, 769 mm.). Calcd. for $C_{11}H_9O_2N$: C, 70.59; H, 4.81: N, 7.49. Found: C, 70.46; H, 4.65; N, 7.42.

Beckmann Rearrangement of its Oxime.—A mixture of the oxime (0.2 g.), glacial acetic acid (1.6 g.) and acetic anhydride (0.4 g.) was saturated with hydrogen chloride gas in the cold and was kept at 100° for three hours in a sealed tube. On cooling, the contents were made alkaline with sodium carbonate and shaken with chloroform. On concentrating the solvent, colorless crystals were obtained; yield, 0.18 g. It formed in colorless flat needles from chloroform, m. p. 216–217.5°. The mixed melting point with an authentic specimen of 5-acetamino-8-hydroxyquinoline (m. p. 217–218°) which had

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[1] Behn, German Patent 95,901 (1897); Rosenmund and Schulz, Arch. *Pharm.*, 265, 308 (1927).

been prepared by acetylation of the 5-amino-8-hydroxyquinoline of Kostanecki[2] gave 217–218°.

Anal. Subs., 2.681: N_2, 0.324 (24.5°, 761.8 mm.). Calcd. for $C_{11}H_{10}O_2N_2$: N, 13.86. Found: N, 13.50.

Acid sulfate gave yellow stout needles from alcohol, m. p. 263° (decomp.).

5-ω-Chloro-acetyl-8-hydroxyquinoline.—This compound was obtained in the same manner as that described for acetylhydroxyquinoline using chloro-acetyl chloride, except that the reaction temperature was kept at 90–95° for seven hours and that the recrystallization was effected by means of warm benzene; yield, 36% of the theoretical. It forms in colorless glistening needles from benzene, m. p. 158–159°. It is fairly easily soluble in the usual organic solvents, dilute mineral acid or caustic soda and moderately soluble in hot water. It gives a green color with ferric chloride and a deep red color with diazotized sulfanilic acid and alkali.

Anal. Subs., 4.984: CO_2, 10.875; H_2O, 1.676. Subs., 4.791: N_2, 0.270 (23.5°, 753 mm.). Calcd. for $C_{11}H_8O_2NCl$: C, 59.59; H, 3.61; N, 6.32. Found: C, 59.51; H, 3.73; N, 6.24.

Reduction of **5-Chloro-acetyl-8-hydroxyquinoline.**—A mixture of 0.15 g. of 5-chloro-acetyl-8-hydroxyquinoline, 1 g. of iron powder and 25 g. of alcohol (80%) with the addition of two drops of hydrochloric acid (10%) was refluxed for three hours. The reaction fluid, after filtration while hot, was evaporated to dryness. On the addition of hydrochloric acid (10%) and trituration, yellowish-white crystals separated out. It was filtered and dissolved in hot water. On addition of sodium acetate to it, colorless flocculent needles separated. These were recrystallized from hot water into colorless needles; m. p. 110–111°; yield, 0.05 g. The mixed melting point with 5-acetyl-8-hydroxyquinoline (m. p. 112–112.5°) gave m. p. 110–112°.

Anal. Subs., 4.022: N_2, 0.269 (22.6°, 758.4 mm.). Calcd. for $C_{11}H_9O_2N$: N, 7.49. Found: N, 7.48.

5-Benzoyl-8-hydroxyquinoline.—Benzoyl chloride (9 g.), 8-hydroxyquinoline (8.7 g.) and aluminum chloride (20 g.) were dissolved in nitrobenzene (80 g.) in the same manner that was described in the previous case. The solution was kept at 110–120° for seven and one-half hours. On cooling, after the addition of ice and hydrochloric acid, the separated nitrobenzene was distilled with steam. Then the separated crystalline mass was filtered, after standing overnight, and washed with hydrochloric acid (10%) until the filtrate became colorless.

It was recrystallized from dilute hydrochloric acid and then the free base was isolated by means of sodium acetate; yield, 11.5 g. (77% of the theoretical). It forms in colorless needles from hot alcohol; m. p. 118–119°. It is fairly easily soluble in the usual organic solvents or in dilute mineral acid, moderately soluble in hot water but difficultly in dilute caustic soda. It gives a green color with ferric chloride and a red color with diazotized sulfanilic acid and alkali.

Anal. Subs., 5.181: CO_2, 14.691; H_2O, 1.967. Subs., 5.152: N_2, 0.261 (21°, 757.7 mm.). Calcd. for $C_{16}H_{11}O_2N$: C, 77.11; H. 4.42; N, 5.62. Found: C, 77.33; H, 4.22; N, 5.73.

Beckmann Rearrangement of its Oxime.—Two-tenths gram of the oxime was treated in exactly the same manner as that described for the rearrangement of the oxime of 5-acetyl-8-hydroxyquinoline; yield. 0.2 g. It forms in yellowish-white small plates from chloroform; m. p. 237–238°. The mixed melting point with an authentic specimen of 5-benzoylamino-8-hydroxyquinoline (m. p. 237–238°) which had been pre-

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[2] Kostanecki, Ber., 24, 152 (1891).

TABLE I

DERIVATIVES OF 5-ACETYL-8-HYDROXYQUINOLINE

Derivative	M. p., °C.	Properties
Hydrochloride	284–285 (dec.)	Yellow cols. from dil. HCl. Hydrolyzes in water
Acid sulfate	248 (dec.)	Yellow needles from alc. Easily sol. in water
Picrate	188–189	Yellow needles from hot water
Chloroplatinate	275 (dec.)	Yellow needles from dil. HCl
Methyl iodide	210 (dec.)	Yellow needles from hot water. Fairly sol. in alcohol or water
Oxime	193	Colorless needles from alc. Fairly sol. in usual organic solvents

Formula	Analyses, % Calcd.	Found	Calcd.	Found
$C_{11}H_9O_2N\cdot HCl\cdot 3H_2O$	HCl 16.33	16.28	H_2O 19.46	19.41
$C_{11}H_9O_2N\cdot H_2SO_4$	H_2SO_4 34.39	34.48		
$C_{11}H_9O_2N\cdot C_6H_3O_7N_3\cdot H_2O$	N 13.46	13.50	H_2O 4.14	4.81
$(C_{11}H_9O_2N\cdot HCl)_2\cdot PtCl_4$	Pt 24.89	24.85		
$C_{11}H_9O_2N\cdot CH_3I\cdot H_2O$	I 38.60	38.27	H_2O 5.19	5.44
$C_{11}H_{10}O_2N_2$	N 13.86	13.89		

TABLE II

DERIVATIVES OF 5-CHLORO-ACETYL-8-HYDROXYQUINOLINE

Derivative	Properties
Hydrochloride	Yellow needles from dil. HCl. Hydrolyzes completely in water
Acid sulfate	Yellow plates from dil. H_2SO_4. Hydrolyzes in water
Picrate	Yellow needles from alcohol
Chloroplatinate	Yellow prisms from dil. HCl

M. p., °C.	Formula	Analyses, % Calcd.	Found
287 (dec.)	$C_{11}H_8O_2NCl\cdot HCl$	HCl 14.15	14.24
263 (dec.)	$C_{11}H_8O_2NCl\cdot H_2SO_4$	H_2SO_4 30.67	30.54
179	$C_{11}H_8O_2NCl\cdot C_6H_3O_7N_3$	N 12.43	12.35
275 (dec.)	$(C_{11}H_8O_2NCl\cdot HCl)_2PtCl_4$	Pt 22.88	22.71

TABLE III

DERIVATIVES OF 5-BENZOYL-8-HYDROXYQUINOLINE

Derivative	Properties
Hydrochloride	Yellow needles from dil. HCl. Hydrolyzes in water
Acid sulfate	Yellow needles from alc. Hydrolyzes in water
Picrate	Yellow needles from alcohol
Methyl iodide	Garnet-colored prisms from hot water. Fairly sol. in hot water
Oxime	Colorless tables from dil. alc. Easily sol. in usual organic solvents

M. p., °C.	Formula	Analyses, % Calcd.	Found
252–260	$C_{16}H_{11}O_2N\cdot HCl$	HCl 12.78	12.72
219–220	$C_{16}H_{11}O_2N\cdot H_2SO_4$	H_2SO_4 28.21	28.38
143–145	$C_{16}H_{11}O_2N\cdot C_6H_3O_7N_3$	N 11.72	11.63
199.5 (dee.)	$C_{16}H_{11}O_2N\cdot CH_3I$	I 32.48	32.33
147–148	$C_{16}H_{12}ON_2$	N 10.61	10.41

pared by benzoylation of 5-amino-8-hydroxyquinoline showed no depression. Moreover, by hydrolysis with hydrochloric acid (20%) the formation of benzoic acid could be ascertained by the mixed melting point method.

Anal. Subs., 3.066: N_2, 0.290 (24°, 766 mm.). Calcd. for $C_{16}H_{12}O_2N_2$: N, 10.61. Found: N, 10.63.

Acid sulfate gave yellow columns from alcohol; m. p. 221–222' (decomp.).

8-Benzoyloxyquinoline.—The benzoylation of 8-hydroxyquinoline with benzoyl chloride was carried out in the presence of pyridine in the cold; yield, 90% of the theoretical after recrystallization. It forms in colorless tables from alcohol; m. p. 122–122.5''.

This compound was prepared first by Bedall by the interaction of 8-hydroxyquinoline and benzoyl chloride at a high temperature; he found a melting point of 118–120° for his product.[3]

Anal. Calcd. for $C_{16}H_{11}O_2N$: N, 5.62. Found: N, 5.54.

The hydrochloride was obtained by treating an ice cold ethereal solution of the free base with dry hydrogen chloride gas. It forms in colorless needles; m. p. 124°. It is easily soluble in water.

Anal. Calcd. for $C_{16}H_{11}O_2N\cdot HCl$: HCl, 12.78. Found: HCl, 12.54.

On submitting this hydrochloride to a Friedel and Crafts reaction, benzoic acid and 8-hydroxyquinoline could be recovered and no condensation product could be isolated.

I hereby desire to express my hearty thanks to Professor Hata for the interest which he has kindly taken in this work and to Mr. C. Sone for his assistance in this investigation.

Summary

The preparation of 5-acetyl-, 5-chloro-acetyl- and 5-benzoyl-8-hydroxyquinoline has been reported.

TOKYO, JAPAN

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE DETERMINATION OF THE STRENGTH OF WEAK BASES AND PSEUDO BASES IN GLACIAL ACETIC ACID SOLUTIONS[1]

BY J. B. CONANT AND T. H. WERNER

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Previous papers of this series have shown that the titration of bases with strong acids in glacial acetic acid solution may be followed by means of the chloranil electrode. We have been interested in extending this study of weak bases to weak pseudo-bases of the type of triphenyl carbinol. It is only by the use of a solvent such as glacial acetic acid that these weak pseudo-bases can be studied and the oxidation–reduction systems composed of free radicals and halochromic salts can be investigated. Before continuing the study of these more strictly organic problems, it was necessary

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[3] Bedall and Fischer, Ber., 14, 1367 (1881).

[1] This is Paper 4 in a series on Superacid Solutions. For earlier papers of this series, see THIS JOURNAL. 49,3047,3062 (1927); and 50,2367 (1928).

to obtain more information in regard to the factors influencing the dissociation constants of weak bases in glacial acetic acid. From the earlier work it was clear that the neutral salt concentration was an important factor. For example, the shape of the titration curves obtained by Hall and Werner[2] clearly pointed to a marked effect of the changing ionic strength on the strength of the base being titrated.

We shall first present in this paper certain results obtained in a study of the effect of the ionic strength on dissociation constants of weak bases in glacial acetic acid solution. The results were obtained by two different methods. One was the electrochemical method using the chloranil electrode in exactly the manner previously described. The other method was to take advantage of the color changes which take place when crystal violet is further neutralized by the addition of strong acids. These changes have been studied in detail in water solution by Adams and Rosenstein.[3] Since the results obtained by the e. m. f. method with colorless bases, and by a spectrophotometric method with crystal violet, are closely related, they will be discussed together.

The results obtained with crystal violet may be considered first. Adams and Rosenstein have proved that the change of color of this substance from violet through blue and green to yellow on adding strong acid, is due to the formation of the green and yellow ions which correspond to the addition of one and two protons, respectively, to the violet ion, according to the equations

$$\underset{\text{violet}}{B^+} + H^+ \rightleftharpoons \underset{\text{green}}{BH^{++}} \qquad (1)$$

$$\underset{\text{green}}{BH^{++}} + H^+ \rightleftharpoons \underset{\text{yellow}}{BH_2^{+++}} \qquad (2)$$

One is thus in a position to evaluate the equilibrium constants for the first and second reactions written above (K_1' and K_2') from spectrophotometric data. Actually, the values of K_2' are subject to a much greater experimental error and the agreement among them we found to be unsatisfactory, and the change of this constant with change in ionic strength was irregular, for reasons which are not entirely clear. For these reasons we shall attempt to interpret only the changes of K_1' with change of ionic strength, giving only an approximate value for K_2'.

Briefly, the method consisted in measuring the extinction coefficients of solutions of crystal violet in buffer solutions of definite ionic strength and measured $P_{\text{H}}^{(\text{HAc})}$. The concentration of dye was so small (4×10^{-6} to 2×10^{-6} molar) that its contribution to the ionic strength could be neglected. The extinction coefficient was measured at intervals of 10 mμ from 470 to 680. From the curves thus obtained with solutions which

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[2] Hall and Werner, THIS JOURNAL, 50, 2367 (1928).

[3] Adams and Rosenstein, *ibid.*, 36, 1452 (1914).

varied from violet ($P_{H}^{(HAc)}$ + 4.75) to yellow (**−3.96**) through blue and green, it is possible to obtain by a process of trial and error the fundamentals corresponding to the extinction coefficients of the violet, the green and the yellow forms (B^+, BH^{++} and BH_2^{+++}). As a first approximation, the molecular extinction coefficients of crystal violet in 3 molar pyridine in glacial acetic acid ($P_{H}^{(HAc)}$ + 4.75) were used for the fundamentals of the violet form and those for the yellow were taken from a 0.05 molar perchloric acid solution in glacial acetic acid. Beyond 540 mμ the absorption due to the yellow species, even if present in large amounts, is practically negligible. Therefore by studying a green solution (by using the appropriate buffer) it is possible to obtain a rough approximation of the green fundamental from the assumed violet fundamental. Finally, the three fundamentals were adjusted by a trial and error method so that the absorption curves obtained with all the fifty solutions yielded satisfactory agreement on the assumption of a certain composition for each solution. Three typical curves are shown in Fig. 1 and the fundamentals finally chosen are given in Table I. It may be noted that the equation for the extinction coefficient of a particular solution at a particular wave length is

$$V\epsilon_v + G\epsilon_G + Y\epsilon_y = \epsilon$$

where ϵ_v, ϵ_G and ϵ_y are the fundamentals and V, G and Y the fraction of the material present in the violet, green and yellow forms. Since there was no evidence of a colorless form, the sum of those fractions was taken as one. The fading, noted by Adams and Rosenstein, which was due to hydrolysis, was not evident in our work because the amount of water present was negligible. The algebraic solution of the above equation is impossible but satisfactory results may be obtained by the laborious trial and error method just described.

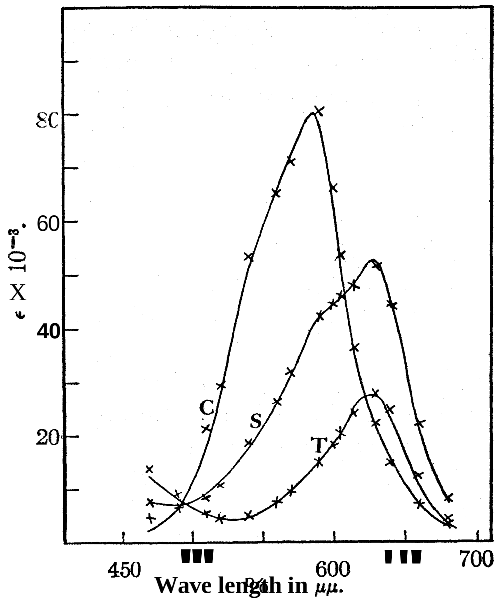

Fig. 1.—Typical absorption curves for crystal violet in acetic acid buffers. Solid lines are experimental curves. Crosses indicate points calculated on assumption of following compositions:

Curve	% Violet	% Green	% Yellow
C	82	8	10
S	20	43	37
T	1	25	74

Expressed logarithmically, the mass law equations for the two equilibria are

$$pK_1' = P_H^{(HAc)} - (\log V - \log G) \qquad (1a)$$
$$pK_2' = P_H^{(HAc)} - (\log G - \log Y) \qquad (2a)$$

The data obtained in the measurements of the $P_H^{(HAc)}$ values are summarized in Table II and the results of the spectrophotometric measurements in Table III.

TABLE I

MOLECULAR EXTINCTION COEFFICIENTS X 10^{-3}

Wave length	Crystal violet in 0.05 *M* $HClO_4$ in HAc	Crystal violet in 3 M pyridine in HAc	Fundamentals chosen for Violet form	Green form	Yellow form
470	19.0	3.01	2.45	...	19.0
490	12.4	8.16	9.40	...	12.8
510	6.15	20.7	25.0	2.0	6.5
520	4.20	31.9	35.0	5.0	4.2
540	1.50	61.0	63.8	13	1.7
560	0.42	77.0	76.6	26	0.5
570	.18	82.7	83.0	36	.18
590	.028	93.2	93.2	56	.028
600	.005	81.3	74.0	69	.005
605	...	68.2	58.0	80	...
615	...	40.8	35.0	95	...
630	...	13.8	16.2	112	...
640	...	7.10	8.47	100	...
660	...	3.20	4.02	50	...
680	...	2.50	2.60	18	...

TABLE II

MEASUREMENTS OF BUFFERS

Soln.	Concn. of base, mole/liter	% Neutral with acid	$P_H^{(HAc)}$	Ionic strength, μ	$\sqrt{\mu}$	pK' of base
			(a) Urea-Sulfuric Acid Buffers			
U1	0.05	6	0.00	0.003	0.055	−1.20
U2	.20	6	+ .37	.012	.110	−0.83
U3	.05	32	− .54	.016	.127	− .87
U4	.20	14	+ .20	.028	.167	− .59
U5	.05	75	−1.00	.0375	.193	− .52
U6	.20	32	−0.03	.064	.253	− .36
U7	.20	50	− .33	.100	.316	− .33
U8	.20	75	− .80	.150	.387	− .32
			(b) Urea-Perchloric Acid Buffers			
U12	0.00025	40	−0.51	0.0001	0.010	−0.69
U13	.003	50	−1.25	.0015	.039	−1.25
U14	.05	7.2	−0.32	.0036	.060	−1.43
U15	.05	13	− .58	.0065	.080	−1.41
U16	.05	39	− .90	.0195	.140	−1.09
U17	.05	50	−1.12	.025	.158	−1.12
U18	.20	45	−0.52	.09	.300	−0.61
U19	.30	50	− .46	.15	.387	− .46

TABLE II (*Concluded*)

(c) Acetoxime–Sulfuric Acid Buffers

Soln.	Concn. of base, mole/liter	% Neutral with acid	$P_H^{(HAc)}$	Ionic strength, μ	$\sqrt{\mu}$	pK' of base
A1	0.00025	40	−0.25	0.0001	0.01	−0.43
A2	.025	40	+ .21	.01	.10	+ .03
A3	.10	40	+ .61	.04	.20	+ .43
A4	.10	80	− .20	.08	.283	+ .40
A5	.10	80	− .24	.08	.283	+ .36
A6	.30	65	+ .42	.195	.44	+ .69

TABLE III

SUMMARY OF MEASUREMENTS OF DISSOCIATION CONSTANTS OF CRYSTAL VIOLET FROM SPECTROPHOTOMETRIC DATA AT 25°

(a) Urea-Sulfuric Acid Buffers

Soln.	Color of solution	$\sqrt{\mu}$	$P_H^{(HAc)}$	Fraction of material as Violet	Green	Yellow	Concn. of crystal violet × 10^6	pK_1'	pK_2'
U2	Blue-violet	0.110	$0.37	0.755	0.22	0.025	1.96	−0.17	−0.57
U4	Blue	.167	+ .20	.440	.40	.16	1.96	+ .16	− .20
U1	Blue-violet	.055	.00	.72	.17	.11	1.96	− .63	− .14
U6	Blue-green	.253	− .03	.17	.45	.38	3.92	+ .39	− .10
U3	Green-blue	.127	− .54	.17	.45	.38	1.96	− .12	− .61
U8	Green	.387	− .80	.004	.132	.864	3.92	+ .72	+ .02
U5	Yellow-green	.193	−1.00	.015	.285	.70	3.92	+ .28	− .61

(b) Urea–Perchloric Acid Buffers

Soln.	Color of solution	$\sqrt{\mu}$	$P_H^{(HAc)}$	Violet	Green	Yellow	Concn. × 10^6	pK_1'	pK_2'
U14	Blue	0.060	−0.32	0.37	0.40	0.23	1.96	−0.29	−0.56
U12	Light blue	.010	− .51	.20	.40	.40	1.96	− .21	− .51
U18	Yellow-green	.300	− .52	.02	.32	.66	3.92	+ .68	− .20
U15	Green-blue	.080	− .58	.20	.465	.335	1.96	− .21	− .72
U16	Yellow-green	.140	− .90	.025	.33	.645	3.92	+ .22	− .61
U17	Yellow-green	.158	−1.12	.01	.25	.74	3.92	+ .28	− .65

(c) Acetoxime–Sulfuric Acid Buffers

Soln.	Color of solution	$\sqrt{\mu}$	$P_H^{(HAc)}$	Violet	Green	Yellow	Concn. × 10^6	pK_1'	pK_2'
A3	Blue	0.20	$0.61	0.59	0.26	0.15	1.96	+0.25	+0.37
A6	Green-blue	.44	+ .42	.20	.43	.37	1.96	+ .75	+ .35
A2	Blue	.10	+ .21	.63	.22	.15	1.96	− .25	+ .04
A4	Green-blue	.283	− .20	.13	.46	.41	1.96	+ .35	− .25
A1	Violet	.01	− .25	.82	.08	.10	1.96	−1.26	− .15

Throughout this paper we have used the same arbitrary convention in regard to the placing of the $P_H^{(HAc)}$ scale as that used in the previous papers of this series. The actual numerical values of the pK's are therefore given in terms of the zero point of that scale. The uncertainty in the reproducibility of the PH values is probably about ±0.02.

The data given in Table III are plotted in Fig. 2. The smooth curves correspond to equations relating pK' and $\sqrt{\mu}$ developed from the fundamental Debye–Hückel Equation **3.**

$$-\log \gamma = \frac{Az^2 \sqrt{\mu}}{1 + Ba \sqrt{\mu}} \qquad (3)$$

Taking the dielectric constant of the medium as 10 and the temperature as 25°, the values of A and B are found to be 11.15 and 0.921×10^8. Substituting we obtain Equation 4

$$-\log \gamma = \frac{11.15 z^2 \sqrt{\mu}}{1 + 0.921 \times 10^8 a \sqrt{\mu}} \qquad (4)$$

Defining the term pK_1 by Equation 5 and substituting the value of $-\log \gamma$ from (4) with appropriate values for z (+1 for z_1 and +2 for z_2), Equation 6 results

$$pK_1 = pK'_1 - \log \frac{\gamma_1}{\gamma_2} \qquad (5)$$

$$pK_1 = pK'_1 - \frac{33.5 \sqrt{\mu}}{1 + 0.921 \times 10^8 a \sqrt{\mu}} \qquad (6)$$

The denominator of the fraction in Equation 6 may be taken as unity for small values of $\sqrt{\mu}$. The resulting equation defines the limiting slope for the change of pK'_1 in dilute solutions; this is shown by line E, Fig. 2. For purposes of comparison, the corresponding slope in aqueous solutions is shown by line A. Applying the limiting equation to the values for pK'_1 obtained in the more dilute solution we estimate pK_1 as -1.7. Substituting this value in Equation 6, and taking "a" as 1.3×10^{-7}, an equation corresponding to Curve B results. Curves C and D were obtained by choosing values of "a" of 1.24 and 1.16×10^{-7}. In deriving Equation 4 the value of the dielectric constant for acetic acid at 25° was taken as 10; the recent measurements of Smyth[4] indicate that the correct value is more nearly 6 for 100% acetic acid. However, since the effect of the presence of salts and a small amount of water (the acetic acid employed in this work melted at 16.4° and contained

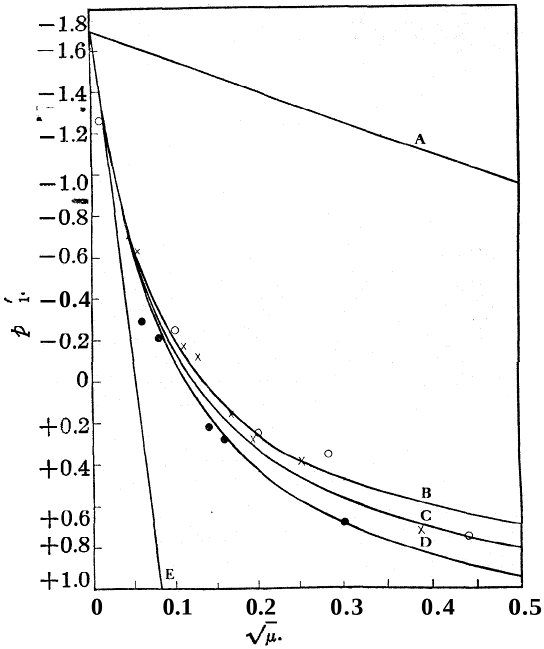

Fig. 2.—Change of pK'_1 for crystal violet with change in ionic strength. A, Theoretical slope for very dilute water solutions; E, theoretical slope for very dilute solutions in glacial acetic acid; B, ○, in acetoxime–sulfuric acid buffers; C, ×, in urea–sulfuric acid buffers; D, ●, in urea–perchloric acid buffers.

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[4] Smyth, This Journal, 52, 1825 (1930).

about *0.2%* of water) is uncertain, we have not thought it worth while to carry through another set of calculations using the dielectric constant of 6. The smaller value would merely give a steeper limiting slope and a different value of *"a"* (essentially an arbitrary constant) would be required in fitting the equation to the experimental points.

The tremendous effect of change of ionic strength on the value pK_1' for crystal violet is evident from Fig. 2. This effect is particularly large in this case, of course, because of the fact that the reaction involves the addition of a proton to a singly charged positive ion with the formation of the doubly charged positive ion. The limiting slope of the Debye theory corresponds to a change of more than 2 PH units for an increase of $\sqrt{\mu}$ from 0 to *0.05.* This is about twenty times the corresponding effect in water, due to the extremely low dielectric constant of glacial acetic acid. However, as a matter of actual fact, the experimental points show a departure from the theoretical limiting slope long before this value is reached, and the total change of pK_1' from the limiting value at $\mu = 0$ to $\sqrt{\mu} = 0.5$ is about 2.6 PH units.

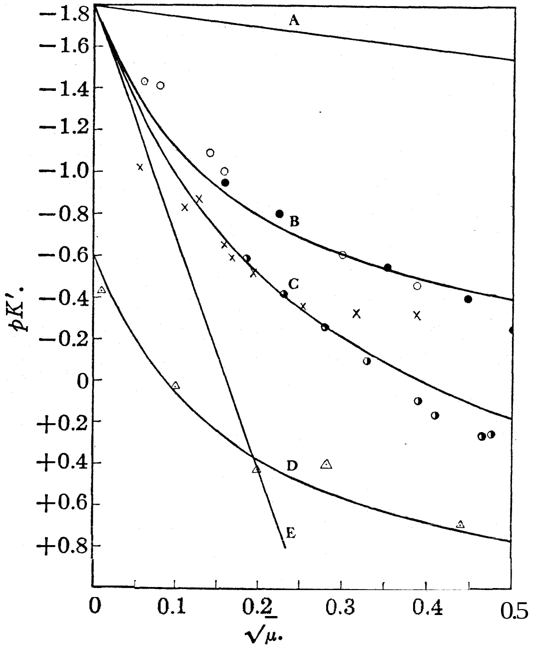

Fig. 3.—Change of pK' for urea and acetoxime with change in ionic strength. A, Theoretical slope for very dilute water solutions; E, theoretical slope for very dilute solutions in glacial acetic acid; B, ○, ●, urea–perchloric acid; C, × ◑, urea–sulfuric acid; D, △, acetoxime-sulfuric acid; ◑, effect of neutral salt (trimethylammonium *p*-toluene sulfonate) on pK' of urea half neutralized with H_2SO_4; ● urea–perchloric acid points from data by Hall and Werner.

The results shown in Fig. 3, which represent the effect of changing ionic strength on the values of pK' for urea and acetoxime, reveal a situation similar to that discussed in the preceding paragraph, except that the limiting slope is here only one-third of that found in the case of crystal violet since the reaction involves the formation of a singly charged ion from a neutral molecule. Neither these results nor those obtained with crystal violet are sufficiently accurate to give a very significant extrapolated value for pK_1 since it is very difficult to obtain measurements in solutions of low ionic strength. In fact, the first value in Section b of Table II has been omitted from Fig, 3 since it is clearly out of line with the other results, presumably because of the difficulties of measuring significant e. m. f.'s with very dilute solutions. In the case of the crystal violet measurements, which were made spectrophotometrically, the solution may be very dilute with respect to the base, but one is dependent on electrical measurements for the $P_H^{(HAc)}$ values of the buffer solutions which must, therefore, be relatively concentrated.

Three different sets of data were used in plotting Fig. 3, as indicated by the symbols. The measurements of the $P_H^{(HAc)}$ values of the buffers employed for the crystal violet work comprised one set; these data are given in Table II. Another set of facts was obtained by adding measured increments of a molar solution of $(CH_3)_3NHSO_3C_6H_4CH_3(p)$ in glacial acetic acid to a 0.05 molar solution of urea in the same solvent half neutralized with sulfuric acid. The ionic strength was calculated as the sum of that contributed by the urea salt and the added neutral salt. The $P_H^{(HAc)}$ was measured in the usual way and since the urea was half neutralized these numbers corresponded directly to the pK'. The third set of values was calculated from the titration of urea with perchloric acid given by Hall and Werner.[2] The value of pK for urea was taken as -1.8 by extrapolation by means of the limiting law Debye equation (Curve E). Curves B and C were drawn from the application of Equations 4 and 5 ($z_1 = 0, z_2 = +1$) and "a" being taken as 0.65 X 10^{-7}, and 0.4 X 10^{-7}, respectively; the equations for Curves B and C were thus

$$pK' = pK + \frac{11.15\sqrt{\mu}}{1 + 5.98\sqrt{\mu}} \tag{7}$$

and

$$pK' = pK + \frac{11.15\sqrt{\mu}}{1 + 3.68\sqrt{\mu}} \tag{8}$$

Curve D for acetoxime was the same as Curve B, the extrapolated value for pK being taken as -0.6.

It is evident from the data summarized in Figs. 2 and 3 that in the more concentrated solutions there are specific effects depending on the nature of the neutral salt. These effects are larger than the corresponding effects in water because of the low dielectric constant of acetic acid. The agreement between the urea–perchloric acid points from the data of Hall and Werner and from Table II is gratifying as showing the reproducibility of our methods. It is clear that both the nature of the cation and anion of the neutral salt are important (divergence of the points on Curves C and D, Fig. 1, and B and C, Fig. 2). The application of these facts to the use of indicators in glacial acetic acid is evident and until the very large "salt effect" with each compound is carefully plotted, conclusions drawn from the use of indicators are only very approximate.

We have been particularly concerned in reducing to a practical working basis our knowledge of strong acids and weak bases in glacial acetic acid with the idea of constructing buffer solutions. The information which we have now obtained from the study of crystal violet, urea and acetoxime, shows clearly the great importance of the ionic strength. In comparing a series of results in buffer solutions, the ionic strength must be constant. If possible, the same neutral salt should be used in every case but even if this is not possible it is better to make all the solutions of the same ionic strength than to neglect this factor. Variations as great as a Ph unit might perhaps be caused by a difference in the nature of the neutral salt, although most of the effects recorded in this paper are only of the order of a few tenths of a Ph unit.

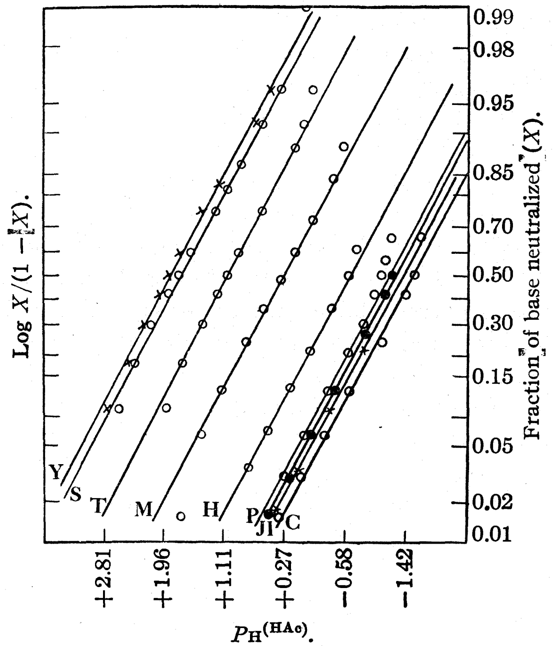

Fig. 4.—Titration curves of bases with sulfuric acid at ionic strength of 0.2 (trimethyl ammonium *p*-toluene sulfonate) plotted on a "Logistic Grid." C, Triphenyl carbinol; I, dianisylcarbinol; J, dianisalacetone; P, acetanilide; H, diphenylanisylcarbinol; M, urea; T, acetoxime; S, o-chloro-aniline; Y, phenylxanthanol.

If the ionic strength is kept constant by employing a relatively large amount of a neutral salt, satisfactory values of pK' can be obtained in a series of experiments. This is illustrated by the results summarized in Table IV for crystal violet in solutions of $\mu = 0.20$. The titration curves of nine bases (including three pseudo bases discussed below) obtained in solutions of $\mu = 0.20$ are plotted in Fig. 4. Since the ionic strength due to the neutral salt (trimethylammonium *p*-toluene sulfonate) is here large compared to the concentration of base (0.05 molar), the increase of ionic strength during the titration is negligible. For this reason the points lie much closer to the theoretical curve than was the case in the investigation by Hall and Werner where no neutral salt was employed. The neutral salt employed in the experiments recorded in Table IV was triethylammonium perchlorate. The values of pK' for urea given in Col. 4 of Table IV vary only slightly more than the probable experimental error; the average value -0.35 ($\sqrt{\mu} = 0.446$) is to be compared with the values of -0.42 and $+0.1$ obtained at the same ionic strength but with the ionic strength contributed by urea perchlorate and trimethylammonium *p*-toluene sulfonate, respectively (Fig. 3). The specific effect of the different neutral salts is evident.

TABLE IV

CONSTANTS FOR CRYSTAL VIOLET OBTAINED WITH BUFFER SOLUTIONS OF CONSTANT IONIC STRENGTH

Temp., 25.0°; μ, 0.200; urea-sulfuric acid mixture (concn. of urea + urea ion = 0.05 molar) with the addition of triethyl ammonium perchlorate.

Base neut., %	Cc. of 0.3 M neutral salt in 50 cc. of buffer	$P_H(HAc)$	pK' of urea	Concn. of crystal violet, moles per liter $\times 10^6$	Fraction of material as Violet	Green	Yellow	pK'_1	pK'_2
95	25.7	−1.22	....	3.92	0.0012	0.105	0.894	0.72	−0.29
75	27.3	−0.74	−0.26	3.92	.007	.220	.773	.76	− .19
50	29.4	− .31	− .31	3.92	.034	.362	.604	.72	− .09
40	30.3	− .19	− .37	3.85	.06	.41	.53	.64	− .08
32	31.0	− .07	− .40	3.77	.08	.44	.48	.67	− .03
14	32.5	+ .42	− .37	1.96	.23	.48	.29	.74	+ .20
6	33.1	+ .80	− .40	1.96	.46	.36	.18	.69	+ .50
0	33.6	+1.59	...	1.96	.88	.11	.009	.69	+ .50

As mentioned earlier in this article, the determination of pK'_2 for crystal violet was not satisfactory. The results have already been given in Tables III and IV. If one plots pK'_2 against $\sqrt{\mu}$ a rather irregular distribution of the points is obtained, the values being more negative in the more dilute solution, as would be expected. The range of values obtained at constant ionic strength is large and we are inclined to attribute the spread to experimental error in determining the percentage of yellow form with its very low extinction coefficient, although there is a regular trend in the data for which we have no explanation.

In connection with the comparison of the dissociation constants of weak bases in water and in acetic acid, it is interesting to consider the results we have obtained with crystal violet and those of Adams and Rosenstein. The values of pK'_1 and pK'_2 in aqueous solution are given by these authors as $+1.94$ and $+1.15$, and we may assume that these are also the values for pK_1 and pK_2 in water. Our extrapolated values are -1.7 and approximately −1.4, although the latter value can hardly be considered of much significance due to the difficulties connected with the measurement of pK'_2. Adams and Rosenstein's value for pK_1 is more positive by about 3.6 units than our value. Taking the value of pK for urea as −1.8 and comparing it with the value in water of about 0, we note that the latter is more positive by about two units. The contrast between water and acetic acid is less with urea than with crystal violet for the reason pointed out by Brönsted,[5] namely, that we are dealing with the reaction $B \longrightarrow BH^+$ instead of $B^+ \longrightarrow BH^{++}$. Any attempt to make correct adjustment between the PH scale in water and acetic acid (if indeed an accurate adjustment is really conceivable),[6] will obviously have to wait until more data can be accumulated which will enable the value of the pK' for different acids and bases in both solvents to be extrapolated to infinitely dilute solution. For practical purposes in the immediate future, we shall continue to use the scale as originally defined, realizing its empirical nature but believing that the position of the zero expresses the qualitative difference between the behavior of solutions of strong acids in water and glacial acetic acid.

Pseudo Bases.—Four of the bases whose titration curves are plotted in Fig. 4 are pseudo bases which react according to the following equation:

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

These are triphenylcarbinol (C), dianisyl carbinol (I), diphenylanisylcarbinol (H), and phenylxanthanol (Y). It is clear that the titration method in glacial acetic acid provides for the first time a method of obtaining really significant values for the basic strength of these very weak pseudo bases. In order to be able to formulate the neutralization of these compounds in the same general scheme as that used for the other bases, we will consider the positive ion in the presence of water as an acid and write the equation

$$pK' = \mathrm{P_H} - \log \frac{[\mathrm{BOH}]}{[\mathrm{B^+}]} + \log \text{(activity of the } H_2O) \qquad (9)$$

Because the compound BOH is a pseudo base, water is necessary for B^+ to be an acid. The strength of B^+ as an acid thus depends on the activity of the water in the solvent. When considering pseudo bases in solutions containing large quantities of water, the activity of the water may be taken as constant; Equation 9 then reduces to the usual form.

In this manner Kolthoff[7] and Lund[8] formulated their interesting results obtained with acetone–water solutions of the polymethoxytriphenyl carbinols. The apparent pK' of a pseudo base measured in acetic acid is a function of the activity of the water according to Equation 10.

[5] Bronsted, *Chem. Reviews*, 5, 295 (1928).

[6] *Cf.* Guggenheim, *J. Phys. Chem.*, 33, 842 (1929).

[7] Kolthoff, THIS JOURNAL, 49, 1218 (1927).

[8] Lund, *ibid.*, 49, 1346 (1927).

$$\text{App. value of } pK' = pK' - \log A_{H_2O} = P_H^{(HAc)} - \log \frac{[BOH]}{[B^+]} \qquad (10)$$

The glacial acetic acid used in the experiments reported in Fig. 4 melted at 16.6° and probably contained an amount of water less than that produced by the neutralization of the pseudo-base.[9] The pK' measurements corresponded to half neutralization of a 0.05 molar solution of the pseudo base so that the total water concentration may be taken as approximately 0.025 (mole fraction, 0.0014). If we assume that in such dilute solutions the activity of the water is equal to its molar concentration, we may approximate the values of pK' from the measured values by subtracting 1.6 units.

If the concentration of water in glacial acetic acid is increased, the measured value of pK' will become more negative according to Equation 10. If this were the only factor involved, the $P_H^{(HAc)}$ value of an equimolecular mixture of BOH and B^+ should become more negative with increasing water content. However, the addition of water to any glacial acetic acid solution of an acid makes the $P_H^{(HAc)}$ value more positive, presumably because of the formation of the H_2OH^+ ion in increasing quantities. Two opposing effects are thus at work; in solutions of very negative $P_H^{(HAc)}$ values the second effect is so marked as to obscure the first entirely, while in all solutions it becomes the predominant factor after the mole fraction of water is about 0.060. The results shown graphically in Fig. 5 illustrate these conclusions. Solutions of a variety of bases (real and pseudo) were titrated with sulfuric acid to the midpoint and then a dilute solution of water added and the change of $P_H^{(HAc)}$ values recorded. The

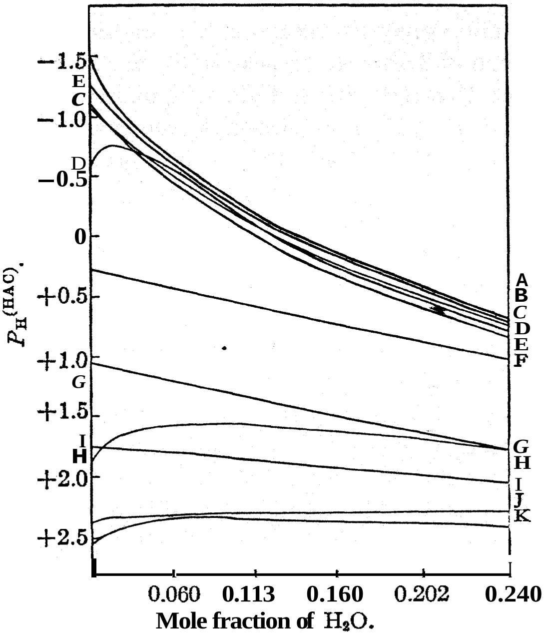

Fig. 5.—Effect of water on bases half neutralized with H_2SO_4. Ionic strength, 0.2. A, Triphenylcarbinol; B, a-naphthyldiphenylcarbinol; C, acetanilide and also dianisal acetone; D, diphenylanisylcarbinol; E, dianisylcarbinol; F, urea; G, acetoxime; H, phenylxanthanol; I, o-chloraniline; J, dinaphthoxanthanol; K, trianisylcarbinol.

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[9] Kendall and Gross, This Journal, 43, 1426 (1921); Webb, *ibid.*, 48, 2265 (1926); Smyth, *ibid.*, 52, 1824 (1930); all give 16.6° as the melting point of pure acetic acid.

ionic strength was 0.2 (the neutral salt was $(CH_3)_3NHSO_3C_6H_4CH_3$) and the initial concentration of the base 0.05 molar. -Four pseudo bases, diphenylanisyl carbinol, phenylxanthanol, dinaphthoxanthanol and trianisylcarbinol, show a decrease and then a rise of $P_{\mathrm{H}}^{(\mathrm{HAc})}$ values with increasing water concentration. With the very weak pseudo bases, triphenylcarbinol, α-naphthyldiphenylcarbinol and dianisylcarbinol, the effect cannot be detected since the decrease of proton activity due to the increased water content predominates from the start. All the real bases show a progressive increase in $P_{\mathrm{H}}^{(\mathrm{HAc})}$ values, as would be expected.

The apparent values of pK' for the pseudo bases we have examined are given in Table V. These values are for 23 ± 1°, 0.05 molar solution of the base titrated with sulfuric acid, ionic strength, 0.2 and glacial acetic acid of m. p. 16.6°. The measure of the basicity by these numbers is independent of any assumptions about color and ionization. In order to evaluate pK, it will be necessary to take into account both the change of pK' with ionic strength and the activity of water in acetic acid. In the case of the stronger bases a further complication results from the fact that the weak second hydrogen of sulfuric acid may be involved; this tends to make the values of pK' too negative.[2] A sulfonic acid would be preferable for titrations of these strong pseudo bases. Further work along these lines is in progress in this Laboratory and the present results must be considered as preliminary. For this reason a discussion of the interesting relationships between structure and pK values will be postponed. It may be noted, however, that our value for trianisylcarbinol (4,4′,4″-trimethoxycarbinol) is +2.6, while the value found by Lund in 50% acetone and water is —0.77. Assuming that the apparent pK' value changes with ionic strength in the same way as with urea (—2 units $\mu = 0.2$ to $\mu = 0$) and that the comparison between water and glacial acetic acid is also the same ($pK^{(\mathrm{H_2O})} - pK^{(\mathrm{HAc})} = +2.0$), it is clear that the two effects cancel. The difference between our value of +2.7 and Lund's —0.77 (a total of 3.5 units) should be a measure of the difference in activity of the water in a 0.025 molar concentration in glacial acetic acid and in 50% aqueous acetone. No data appear to be

TABLE V

SUMMARY OF APPARENT pK' VALUES OF CERTAIN PSEUDO BASES AT 25° IN GLACIAL ACETIC ACID, M. P. 16.6°. BASES IN 0.05 MOLAR SOLUTION TITRATED WITH SULFURIC ACID $\mu = 0.2$ WITH $(CH_3)_3NHSO_3C_6H_4CH_3(p)$

Name	Formula	Apparent pK'
Triphenylcarbinol	$(C_6H_5)_3COH$	−1.47
α-Naphthyldiphenylcarbinol	$(C_{10}H_7)(C_6H_5)_2COH$	−1.25
Dianisylcarbinol	$(C_6H_4OCH_3)_2HCOH$	−1.14
Diphenylanisylcarbinol	$(C_6H_5)_2(C_6H_4OCH_3)COH$	−0.59
Phenylxanthanol	$(C_6H_4)_2O(C_6H_5)COH$	+1.91
Dinaphthoxanthanol	$(C_{10}H_6)_2OCHOH$	+2.40
Trianisylcarbinol	$(C_6H_4OCH_3)_3COH$	+2.56

available to check this but the direction of the effect is correct and the order of magnitude seems reasonable.

Experimental

(a) Materials.—The acetic acid was purified by repeated freezing of redistilled commercial synthetic acetic acid. The melting point was 16.4° except in the work with the pseudo bases when material of m. p. 16.6° was employed. Anhydrous perchloric acid was prepared from 60% aqueous acid and acetic anhydride as previously described. The solution of sulfuric acid in glacial acetic acid was prepared from 99.9% sulfuric acid. It was standardized by electrometric titration in glacial acetic acid with sodium acetate. The crystal violet employed was Dr. Grübler's "Höchst" brand. Its absorption spectrum was determined in aqueous solution and was found to be identical with that given by Adams and Rosenstein within our experimental error.

All the organic substances used in this work except the "neutral salts" are familiar compounds easily purified and characterized by their melting points; no description of them is therefore required. The neutral salts were prepared by passing the amine into a water solution of the acid, evaporating to dryness in vacuum and drying over phosphorus pentoxide. Both substances were colorless crystalline solids.

(b) Apparatus.—The spectrophotometer employed was a Keuffel and Esser color analyzer. Its adjustment was tested by means of a blue and yellow glass whose extinction coefficients over a wide range had been determined by the Bureau of Standards. The solution was placed in a 10-cm. glass cell with fused glass ends; a cell of the same length containing acetic acid was placed in the comparison beam. The temperature was kept at 25 ± 0.3°. Three readings were taken at each wave length and averaged.

The electrometric measurements were made with a cell similar to that previously used but so constructed that only 10 cc. instead of 50 cc. could be employed. It is shown in Fig. 6; a micro-buret was used in the titrations. The temperature was 23 ± 1°. The $P_{\mathrm{H}}^{(\mathrm{HAc})}$ values were obtained from the measured e. m. f. (E) by the equation previously employed.

$$P_{\mathrm{H}}^{(\mathrm{HAc})} = \frac{0.566 - E}{0.059}$$

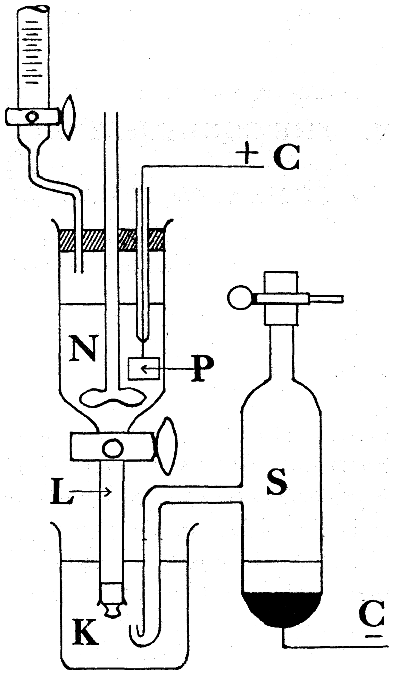

Fig. 6.—Cell for titrations in glacial acetic acid using chloranil electrode. S, Saturated calomel electrode; K, saturated KCl in water; L, LiCl in acetic acid; N, 10 cc. of solution to be measured; P, platinum electrode; C, connections to electrometer and potentiometer.

Summary

1. A spectrophotometric study has been made of the acid–base equilibria in solutions of crystal violet in buffered glacial acetic acid solutions.

2. **An** electrometric study of a number of weak bases and pseudo bases in glacial acetic acid has revealed the large effect of changing ionic strength **which** was also noted in the spectrophotometric study.

3. The effect of added water on the apparent constants of a number of **weak** pseudo bases has been investigated and a method outlined for obtaining significant values for the relative basicity of the "halochromic" carbinols.

CAMBRIDGE, MASSACHUSETTS

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

V. THE CONDENSATION OF HYDROCARBONS BY ELECTRICAL DISCHARGE.

COMPARISON WITH CONDENSATION BY ALPHA RAYS[1]

BY S. C. LIND[2] AND GEORGE GLOCKLER[3]

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In a former paper[4] it has been shown that the condensation of ethane by electrical discharge in an ozonizer is in many ways similar to the same reaction when produced by the ionization due to the alpha particles from radon.[5] The experiments have now been extended to the gases methane, propane, butane and ethylene. It has been found *that there exists a similarity in the condensations as produced by the ionization due to α-particles and by electrical discharge in an ozonizer* for all the gases studied. It is the object of the present paper to describe these experiments and to discuss certain experimentally determined ratios which support the statement made. The experiments on ethane have been repeated with the new apparatus and confirm the former study. They are included for the sake of completeness and for comparison.

Experimental Procedure

The apparatus used to study these condensations is shown in Fig. 1 and consists of an all-glass pyrex ozonizer, a Liebig condenser and a manometer. The system as a whole is of the circuit type and a slight circulation was probably attained by the thermal siphon principle since the ozonizer would naturally heat up (to about 40°) during a run due to power losses and since the condenser kept the other leg of the system cold, by

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[2] Director of Project No. 8.

[3] American Petroleum Institute Research Associate.

[4] S. C. Lind and George Glockler, *Trans. Am. Electrochem. Soc.*, 52, 3746 (1927).

[5] S. C. Lind and D. C. Bardwell, THIS JOURNAL, **48**, 2335–2351 (1926).

having tap water (18°) running through it. The pressure in the ozonizer changes on account of the changes of temperature due to the reaction. A correction of 12 mm. was applied at the maximum pressure, which was determined by noting the pressure drop in the butane reaction that occurred when the reaction had been stopped near the maximum pressure when the system was allowed to cool to room temperature (Fig. 3). The drop in pressure at the end of the experiments due to cooling was noted to be about 10 mm. and these two corrections were applied to the curves shown in Fig. 2. The trap at the bottom of the ozonizer should catch any liquid condensates and was also used in the first step of the fractional distillation of the gases resulting from the condensations. The ozonizer proper was placed into the circulating system by means of two ground seals (stopcock grease and mercury-seals) in such a manner that it could easily be removed for cleaning before each run. The electrical set-up consisted of a Thordarson Transformer which would furnish about 18,000 volts to the ozonizer with 94 volts and 7.4 amperes in its primary. The electrical conditions were kept constant at these values during all the experiments. The first series of experiments consisted of runs of eight and one-half hours' duration. The pressure changes were observed during the whole period and after the conclusion of each experiment the remaining gases were analyzed for hydrogen, methane, ethane, propane, butane and pentane by fractional distillation, beginning at liquid-air temperatures. The hydrogen in the hydrogen–methane mixture was removed by diffusion through a palladium tube. The remaining methane was checked by combustion and a correction applied for any ethane that might have been pumped off with the hydrogen–methane fraction. Ethane was distilled off at −150°, propane at −120° and butane at −90°. The remaining gas was taken to be pentane. The liquid composition (empirical formula) could be determined from these gas analyses by constructing an "atomic balance sheet." It is possible to find the number of carbon and hydrogen atoms that must have gone into the liquid condensate from the amount of hydrocarbon used, its composition and the

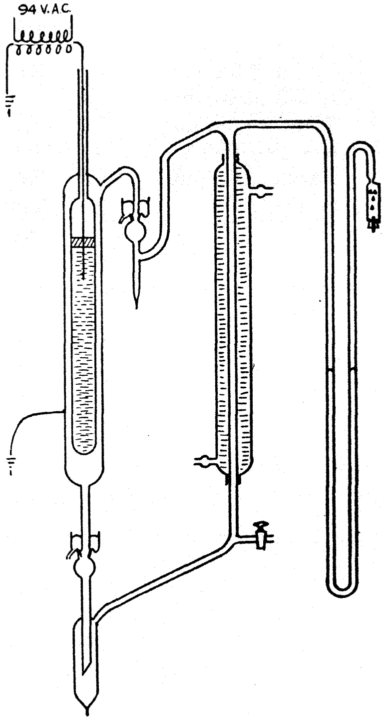

Fig. 1.—Apparatus.

TABLE I

GAS ANALYSIS OF THE HYDROCARBONS USED

	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_2H_4
CH_4	100.0	...	...	...	...
C_2H_6	...	98.0	0.5	...	...
C_3H_8	...	2.0	99.1	1.0	0.3
C_4H_{10}	...	...	0.4	97.2	1.4
C_2H_4	...	...	...	...	98.5
C_5H_{12}	...	...	...	1.8	...
	100.0	100.0	100.0	100.0	100.2

analyses of the resulting gases. The initial gases were obtained from commercial sources except methane, which was prepared from sodium acetate. They were reasonably pure as the following analysis (by fractionation) shows.

These gases were distilled into the apparatus and any permanent gases were pumped off. The experimental results are shown in Table II, which contains the average of at least two experiments carried out with each gas. It was always possible to obtain graphs of **the** "pressure–time **relation**" which checked very satisfactorily indeed, showing that the experiments are entirely reproducible. In Col. 4 of Table II the details of a

TABLE II

EXPERIMENTAL DATA

Gas used	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_4H_{10}	C_2H_4
Initial volume, cc.	232	229	228	231	231	222
Initial press., mm.	759	754	753	762	756	744
Time of run, min.	510	480	510	80	510	400
Reaction volume, cc.	238	238	238	238	238	234
Final press., mm.	759	754	787	873	808	215
Final H_2, cc.	143	147	143	65	148	47
CH_4	64	43	36	41	37	8
C_2H_2	...	...	...	1		
C_2H_4	...	...	...	5	...	...
C_2H_6	13	28	42	14	38	3
C_3H_8	5	4	16	13	10	1
C_4H_{10}	2	4	2	127	14	2
C_5H_{12}	3	...	2	...	3	...
Final gases, cc.	233	226	242	264	247	60

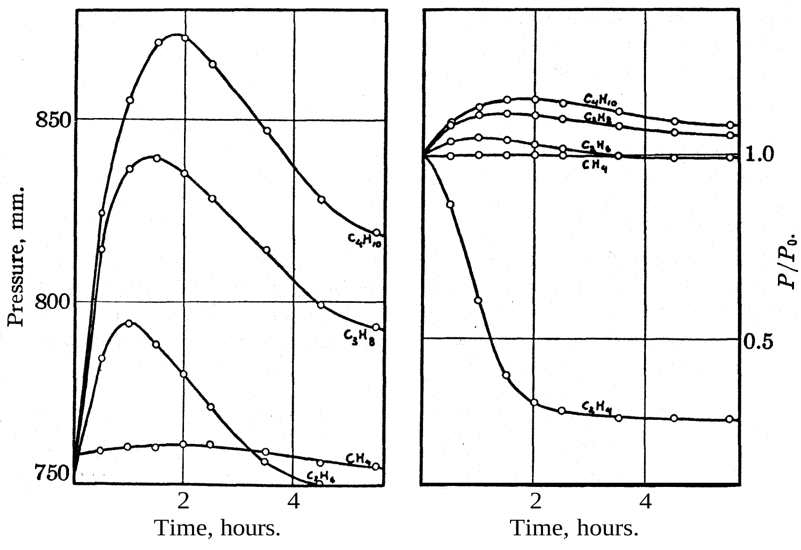

Fig. 2.—Pressure changes during condensation in an ozonizer.

short run (eighty minutes) on butane are given, which was stopped at the maximum pressure attained during the longer (510-minute) run. This experiment was performed to find out whether or not unsaturates are formed during the reaction. This point will be discussed later. The detailed runs are shown in Figs. 2 and 3.

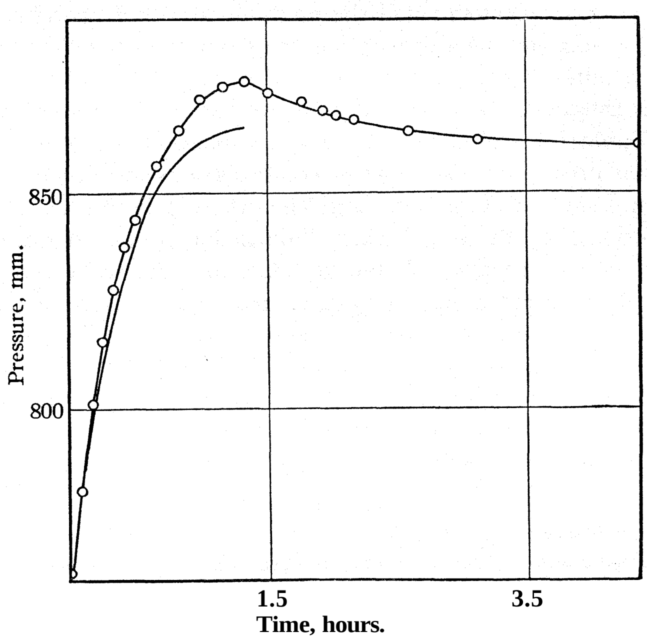

Fig. 3.—Pressure changes during a short (80-minute) run with butane, showing temperature effect.

Discussion of Results

1. The Pressure Changes during Reaction.—It is seen that the saturated hydrocarbons all show the same general pressure change as the reaction proceeds in time. They all show a maximum pressure one to two hours after the beginning of the reaction. Especially remarkable is the decrease of pressure during the later stages of the reaction. The one unsaturated hydrocarbon tried (ethylene) shows a decrease in pressure to about one-third of the initial pressure. Since the object of the present research is a comparison of the alpha-ray condensations of the hydrocarbons with the same reactions produced by electrical discharge in an ozonizer, the data of Lind and Bardwell[6] of the alpha-ray condensations have been recalculated and replotted so as to be easily comparable with the present material.

In the case of the saturated hydrocarbons the a-ray experiments were

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[6] **Reference 5 and also THIS JOURNAL, 48, 1556 (1926).**

carried out in stages in such a manner that at the end of each period hydrogen and methane were pumped off. When the data are inspected it is seen that in the case of butane a slight increase in pressure is noticeable. In order to compare the pressure data with the present experiments, it was assumed that during each interval the pressure would have increased the same proportionate amount had the methane and hydrogen been present. This assumption may be a drastic one but the object is only to show that there is a slight increase in pressure during the alpha-ray condensations and this is immediately apparent from the data. The essential data are given in Table III and in Fig. 4. For comparison the pressure changes (final/initial press.) for the ozonizer condensations are given for the first ninety minutes of reaction. It should be noted that the abscissas for the radon reaction are "the time" where "ionization produced since the commencement of the reaction" should be taken in order to be comparable to the corresponding curves for the ozonizer reactions. Since in the ozonizer reactions it may be assumed that a constant current was flowing producing a definite ionization the total ionization may be taken proportional to the time. It was not thought necessary to reduce the alpha-ray reactions since this would merely result in a relative shortening of the abscissas. The only thing of interest was the general picture showing the relative pressure

TABLE III

PRESSURE CHANGES IN THE RADON CONDENSATIONS OF THE SATURATED HYDROCARBONS,[5] FOR COMPARISON WITH THE OZONIZER REACTIONS

Gas	$1 - e^{-\lambda t}$	Time	Pressure	(Mm. Hg)	P/P_0
CH_4	0	0	....	730	1.000
	0.144	17 h	....	729	0.999
	.290	1 d 21 h	729(641/640)	730	1.000
	.490	3 d 16 h	730(610/609)	731	1.001
	.703	6 d 16 h	731(570/568)	732	1.003
C_2H_6	0	0	....	1266	1.000
	0.038	3.5 h	....	1266	1.000
	.159	22 h	1266(1244/1245)	1265	0.999
	.301	1 d 22 h	1265(1179/1175)	1269	1.003
	.415	2 d 22 h	1269(1089/1087)	1272	1.006
C_3H_8	0	0	....	830	1.000
	0.134	17 h	....	830	1.000
	.278	1 d 19 h	830(794/787)	837	1.008
	.393	2 d 18 h	837(740/735)	845	1.018
	.577	4 d 18 h	845(703/691)	860	1.035
	.752	7 d 17 h	860(644/633)	875	1.053
C_4H_{10}	0	0	....	826	1.000
	0.152	21.5 h	....	831	1.007
	.267	1 d 17 h	831(725/717)	838	1.017
	.388	2 d 17 h	838(652/642)	858	1.038
	.489	3 d 17 h	858(591/577)	880	1.066
	.703	6 d 17 h	880(557/529)	928	1.125

changes in the case of the two types of condensation and it is seen that there is a comparable increase in pressure in these two modes of condensation. It is believed then that the curves of pressure increase as a function of time of reaction establish the first point of our thesis: that *there is for the saturated hydrocarbons an analogy in their pressure changes during reaction when under the influence of the two activating agents.*

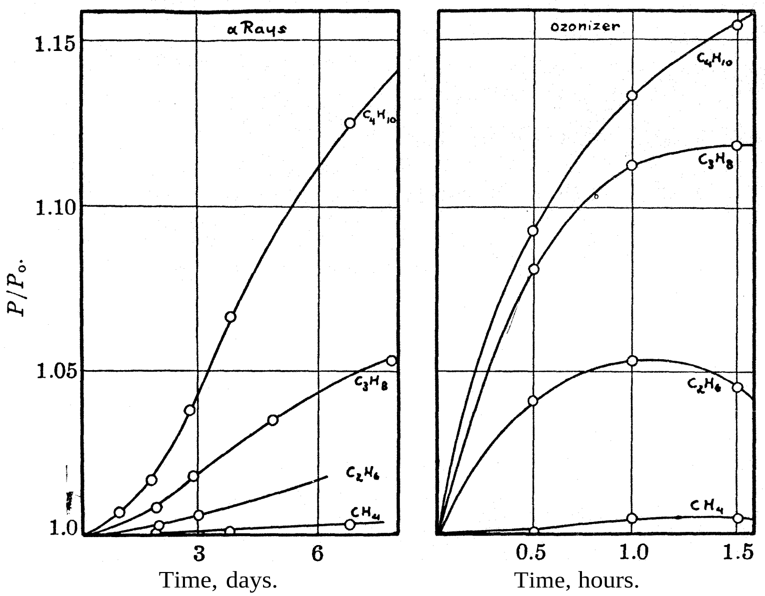

Fig. 4.—Comparison pressure changes in the alpha ray and ozonizer condensations for saturated hydrocarbons.

In an entirely similar manner it has been found that the pressure decreases during the condensation of the unsaturated ethylene both when reaction is brought about by the activation due to alpha rays and in electrical discharge in an ozonizer. Here the data of Lind, Bardwell and Perry[6] were rearranged as shown in Table IV and the comparison is made in Fig. 5 with the data of the present experiments. In the case of the condensation of ethylene it is seen from Fig. 5 that the relation between (P/P_0) and the total ionization is a straight line, showing in a graphical way that the M/N ratio is constant during the reaction. While the two curves show the same general trend (a decrease in pressure to about one-third the initial pressure), they are not of the same shape. This may mean a difference in the detailed mechanism of the two reactions and needs further investigation. For the present purpose only the most obvious features are to be considered.

The main point is: *both condensations of ethylene show a pressure decrease to about one-third the initial pressure.*

TABLE IV

PRESSURE CHANGES IN THE RADON CONDENSATION OF ETHYLENE[6]

$1 - e^{-\lambda t}$	$iP/760$				$\Delta(1 - e^{-\lambda t}) \times \frac{iP}{760}$		Ionization	P/P_0
	C_2H_4	H_2	CH_4	Total				
0	2.19	0	0	2.19			....	1.000
					0.0386 X 2.05	0.0792		
0.0386	1.90	0.0062	0.0029	1.91			0.0792	0.882
					.0114 X 1.86	.0212		
.0500	1.80	.0081	.0038	1.81			.1004	.850
					.0697 X 1.60	.1130		
.1197	1.35	.0196	.0092	1.38			.2134	.684
					.0217 X 1.32	.0287		
.1414	1.22	.0236	.0109	1.26			.2421	.640
					.0260 X 1.20	.0312		
.1674	1.10	.0275	.0129	1.14			.2733	.600
					.0314 X 1.07	.0365		
.2015	0.95	.0320	.0151	1.00			.3098	.540
					.0632 X 0.88	.0557		
.2647	.70	.0410	.0195	.76			.3655	.470
					.1381 X .60	.0830		
.4028	.36	.0540	.0261	.44			.4485	.370
					.1791 X .36	.0620		
.5747	.17	.0675	.0318	.27			.5105	.320
					.2345 X .27	.0646		
.7142	.15	.0778	.0366	.27			.5751	.350
					.2858 X .25	.0715		
1.000	.09	.0983	.0420	.23			.6466	,390

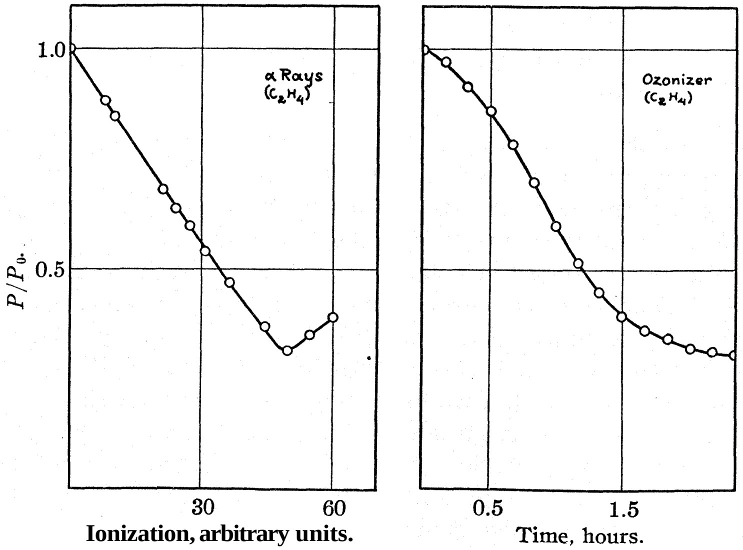

Fig. 5.—Comparison of pressure changes in the alpha ray and ozonizer condensations for ethylene.

The study relating to pressure changes can be made in another way by comparing the volume changes during the two condensations **and** the ratios of the final to the initial pressure and the maximum to the initial pressure. The pertinent data are collected in Table V. It is seen that the same general trend exists for both types of reactions (Col. **3** to be compared with Cols. 4 and 5).

TABLE V

PRESSURE RELATIONS. COMPARISON OF RADON AND OZONIZER CONDENSATIONS OF HYDROCARBONS

	Volume relations			Pressure relations	
Gas	Final other gases, cc. (I)	Hydrocarbon used, cc. (II)	Ratio $\frac{\text{Col I}}{\text{Col. II}}$ (III)	$\frac{P_{\text{final}}}{P_{\text{initial}}}$ (IV)	$\frac{P_{\text{max.}}}{P_{\text{initial}}}$ (V)
		Radon Condensation			
CH_4	5.63	5.56	1.01	...	..
C_2H_6	15.92	14.58	1.09	...	..
C_3H_8	19.50	17.07	1.14		
C_4H_{10}	28.09	24.69	1.13	...	.
C_2H_4	...	...	...	0.323	.
		Ozonizer Reaction			
CH_4	169	168	0.998	1.00	1.03
C_2H_6	198	201	.985	0.99	1.07
C_3H_8	226	212	1.060	1.05	1.14
C_4H_{10}	233	217	1.07	1.07	1.16
C_2H_4	60	222	0.27	0.29	..

2. **Free Hydrogen Production.—A** further point **of** comparison between the alpha ray and the ozonizer condensations is the "free hydrogen production" as related to the amount of initial hydrocaron reacted. This quantity may also be expressed as the ratio ($-\Delta$H.C./ΔH_2) "hydrocarbon disappearing to hydrogen appearing." The necessary data for its calculation are given in Table VI and for the alpha-ray reactions the figures are taken from the work of Lind and Bardwell.[5] It should be

TABLE VI

FREE HYDROGEN PRODUCTION

Analysis of free hydrogen production of saturated hydrocarbons by electrical discharge (ozonizer) and comparison with alpha-ray reaction.[5]

		CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_2H_4
Initial gas (cc. N. T. P.) taken		231.5	229.4	228.1	231.0	222.2
% of gas reacted		72.7	87.6	93.0	94.5	100.0
H_2 of init. gas reacted (cc. N. T. P.)		167 X 2	201 X 3	212 X 4	218 X 5	222.2 X 2
Free hydrogen (ozonizer)		143	147	143	148	47
From ozonizer reaction % = (Free H_2 X 100)/(H of init. H. C. reacted)		42.8	24.4	16.8	13.6	10.6
The same % (a-reaction)		37.8	25.5	16.1	13.9	11.9
$\frac{-\Delta HC}{\Delta H_2}$	α	1.32	1.31	1.54	1.44	4.18
	oz.	1.17	1.37	1.44	1.60	4.70

noted that the two modes of expressing the "free hydrogen appearing during the reaction" are related as follows:

$-\Delta \text{H.C.}/\Delta H_2 = 1/(\text{free H} \times n)$, where $n = 2,3,4,5$ for CH_4, C_2H_6 C_3H_8 and C_4H_{10}, respectively.

By comparing lines five and six and lines seven and eight of Table VI it is seen that these ratios are the same for both types of condensations.

The second point in our argument that the condensations of hydrocarbons by alpha rays and by electrical discharge are similar reactions is then: *"the amount of free hydrogen produced is of the same order in both types of condensations."* The ratio in question changes to a larger value (about 4) for the unsaturated ethylene.

3. The Percentage of Hydrogen in the Hydrogen–Methane Fraction.—The ratio $\Delta H_2/\Delta(H_2 + CH_4)$ was calculated from the data on gas analysis of the gases after the condensation. It is seen (Table VIII) that the percentage of hydrogen in the hydrogen–methane mixture is about 80% for the reactions of the saturated hydrocarbons and a little greater (86%) for the unsaturated ethylene. The comparison with the similar data on the alpha-ray reaction shows that *in both types of condensation hydrogen and methane appear in the same relative amounts.*

4. Percentage of Liquid Conversion.—The fraction of the hydrocarbon that has undergone reaction which appears as liquid product is seen to be greater in the order: methane, ethane, propane, butane and ethylene. Again this behavior is the same for both kinds of reaction and it may be said that it appears to be easier to convert these hydrocarbons into liquid in the order given.

5. The Liquid Composition.—As has been noted above, it is possible to calculate the average empirical composition of the liquid product from the gas analysis of the reaction products. This calculation has been carried out from the data of Table II and the results are given in Table VIII. It is seen that the average composition of the liquid mixture cor-

TABLE VII

ATOMIC BALANCE SHEET FOR CONDENSATION OF ETHYLENE[6] BY RADON

$$\text{Any gas volume (N. T. P.)} = V_0 = \text{V (reaction vessel)} \times \frac{273}{298} \times \frac{P}{760} = K \times P$$

	Carbon	Hydrogen
H_2	....	$K \times 218 \times 2$
CH_4	$K \times 24.2 \times 1$	$K \times 24.2 \times 4$
C_2H_4	$K \times 80.0 \times 2$	$K \times 80.0 \times 4$
	$K \times 184.2$	$K \times 852.8$
Initial gas	$K \times 1992.0$	$K \times 3984.0$
Liquid phase	$K \times 1907.8$	$K \times 3131.2$

$$\text{Liquid composition} = \frac{3131.2}{1907.8} = 1.65 \text{ or } C_nH_{1.65n}$$

TABLE VIII

CONDENSATION OF FIVE HYDROCARBONS IN ELECTRICAL DISCHARGE: (SUMMARY OF RESULTS AND COMPARISON WITH ALPHA-RAY CONDENSATIONS)

	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_2H_4
(1) Pressure Changes					
Final press./initial press. (ozonizer)	1.00	0.99	1.05	1.07	0.29
Final vol./H. C. used (ozonizer)	1.00	0.99	1.06	1.07	.27
Max. press./init. press. (ozonizer)	1.03	1.07	1.14	1.16	..
Final vol./vol. H. C. used (alpha rays)	1.01	1.09	1.14	1.13	.32
(2) Free Hydrogen					
$\Delta(\Delta H.C./\Delta H_2)$ **(ozonizer)**	1.17	1.37	1.44	1.50	4.70
$\Delta(\Delta H.C./\Delta H_2)$ **(alpha rays)**	1.32	1.31	1.54	1.44	4.18
(3) Hydrogen–Methane Ratio					
$\Delta H_2/\Delta(H_2 + CH_4)$ **(ozonizer)**	..	0.77	0.80	0.80	0.86
$\Delta H_2/\Delta(H_2 + CH_4)$ **(alpha rays)**	..	.83	.79	.84	.90
(4) Liquid Conversion					
Per cent. (ozonizer)	54	77	74	77	93
Per cent. (alpha rays)	30	56	52	71	96
(5) Liquid Composition					
Empirical formula (ozonizer)	C_nH_{2n}	C_nH_{2n}	C_nH_{2n}	C_nH_{2n}	$C_nH_{1.7n}$
Empirical formula (alpha rays)	C_nH_{2n}	$C_nH_{1.9n}$	$C_nH_{1.8n}$	$C_nH_{1.9n}$	$C_nH_{1.7n}$
(6) Hydrocarbon Reacted					
Per cent. (ozonizer)	73	88	93	95	100
Per cent. (alpha rays)	18	27	45	68	92

responds to an empirical formula C_nH_{2n} for the saturated hydrocarbons and to $C_nH_{1.7n}$ for the unsaturated ethylene. Similar results have been obtained for the alpha-ray reactions, as is shown in Table VIII. The composition of the liquid condensate derived from ethylene by alpha-ray condensation has been calculated as shown in Table VIII. Another point of similarity has thus been established: *The empirical composition of the liquid mixtures derived from both types of condensations is the same.*

6. Total Hydrocarbon Reacted.—The percentage of the total hydrocarbon reacted in a given interval of time under similar conditions is greater in the order given above. The same order is found in the alpha-ray reactions. However, these factors are not comparable since the radon reactions were not carried so far toward completion as the ozonizer reactions; but the data do fit into the general picture very well and again it can be said that both reactions show the same general trend.

7. Statement of Results.—The factors studied have been collected in Table VIII and it is believed that the data shown there support the thesis which it is expected to prove: *"for all of the hydrocarbons studied the condensations by alpha rays and in electrical discharge have many points in common, which lead to the belief that they both are brought about by the same agency."*

8. Mechanism of Reaction.—The question which remains to be answered is: What is the mechanism of these condensations? On the ion-cluster theory the following steps should be taking place: (1) the formation of an ion; (2) the formation of a cluster; (3) the formation of a larger hydrocarbon molecule with elimination of hydrogen and methane; (4) the ionization of the larger molecule by direct electron impact; (5) the formation of an ion of the larger molecule by electron transfer. This mode of ionization is important because it favors the larger molecules for reaction.

On the basis of these reaction steps it is possible to construct many reaction schemes which will conform to the data of Table VIII. It is easily seen that the possibilities for splitting, rebuilding and rearrangements under the above reaction plan are enormous for any of the hydrocarbons investigated and no satisfactory reaction mechanism can be given unless *all* of the reaction products have been determined. This would mean that not only must the gaseous reaction products be completely analyzed but also the liquid condensation products. As is well known, the analytical difficulties in the separation of the hydrocarbons are considerable. Even if such analyses were made it must be realized that all of the products of the initial reaction except hydrogen condense in a similar manner and in some cases even more readily than does the initial hydrocarbon. This makes the whole problem one of great complexity and while it has been possible to derive a series of reaction schemes which have the advantage of simplicity, uniformity, compliance with the empirical reaction rules laid down above, we prefer to postpone the discussion to a later date when more analytical data have been procured and shorter runs have been studied. The mechanism of these condensations may be studied by shortening the reaction period, so that the initial reaction products are obtained before they have been changed. This method was employed with butane and it appears that unsaturates are formed during the reaction. However, we have only initiated this study and much more work needs to be done.

9. Unsaturates in the Gas Phase.—While it has been found that the average composition of the liquid condensates corresponds to an olefin, no indication has been found that there existed unsaturates in the gas phase at the end of the eight and one-half hour runs. The fractionations carried out on the gaseous reaction products always showed fractions of hydrocarbons which corresponded closely in vapor pressure to the saturated hydrocarbons. However, one experiment on butane was stopped with eighty minutes' duration (Fig. 3) and the pressure had then reached the maximum pressure recorded in the former experiment. The analysis by fractionation showed at once that fractions were now present of different vapor pressures from those obtained previously. Ethylene and acetylene thus appear to exist in the gas phase. The disappearance of these unsatu-

rates during the later stages of the reaction may be the cause of the pressure drop observed. In our further work it is expected to study the composition of the reaction products obtained in runs of short duration where the total pressure has reached the maximum pressure of the longer runs. It is hoped that information from these and even shorter runs may help in the derivation of a possible reaction scheme for these condensations.

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Summary

The condensation of methane, ethane, propane, butane and ethylene has been studied in electrical discharge. It has been found that these reactions are quite similar to the condensations caused by alpha rays. The following factors give evidence of this similarity of reaction: (1) the pressure changes as a function of the time; (2) the free hydrogen produced during the reaction; (3) the relative amount of hydrogen and methane in the hydrogen–methane fraction of the resultant gases; (4) the percentage of liquid conversion; (5) the average composition of liquid condensate; (6) the percentage of the hydrocarbons reacted All of these factors are quite similar for both types of condensation and it is argued that both types of reaction must be caused by the same mechanism. A reaction scheme is discussed on the basis of the ion cluster theory. The usual ideas are amplified in one respect in that it is assumed that the larger molecules are ionized not only by electron impact but also by electron exchange.

MINNEAPOLIS, MINNESOTA

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

THE COMPOSITION AND STRUCTURE OF MESQUITE GUM[1]

BY ERNEST ANDERSON AND LOUISE OTIS

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Previous investigations[2] have shown that mesquite gum yields 2-arabinose and d-galactose on hydrolysis and that it contains a hexose uronic acid. When the work described in this article was begun, the gum was assumed to be the salt of a complex organic acid composed of the above substances. This investigation has established the presence of methanol and *d*-glucuronic acid as constituents of the gum and has shown conclusively that it

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[1] The material in this article is extracted from a thesis submitted by Louise Otis in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Northwestern University.

[2] C. Morfit, *Am. J. Sci.*, 19, 264 (1855); R. H. Forbes, "The Mesquite Tree: Its Products and Uses," Arizona Agricultural Experiment Station, Bulletin No. 13 (1895); E. Anderson, L. Sands and N. Sturgis, *Am. J. Pharm.*, 97, 589 (1925); E. Anderson and L. Sands, *Ind. Eng. Chem.*, 17, 1257 (1925); THIS JOURNAL, 48, 3172 (1926).

is the salt of an organic acid composed of four molecules of Earabinose, three molecules of d-galactose, one molecule of methanol and one molecule of d-glucuronic acid, combined with the loss of eight molecules of water.

During the course of the research the free monobasic acid of which mesquite gum is a salt, was prepared and analyzed. This complex molecule was then hydrolyzed in 3% sulfuric acid, first at 80° and finally in the autoclave at fourteen pounds' pressure. This process gave successively less complex monobasic acids, which were isolated in the form of calcium salts and analyzed. From a study of the composition and reactions of the various products isolated it is possible to deduce some facts in regard to the method of linkage of the original molecule.

Identification of an Ether Linked Methoxy Group in Mesquite Gum.—It was shown by von Fellenberg[3] that a glucosidic methoxy group can be removed from naturally occurring compounds by heating at 80 to 90° with a 2% solution of sodium hydroxide. An ether linked methoxy group, on the other hand, cannot be removed by the above method but is removed by mixing the compound with 72% sulfuric acid and boiling for ten minutes. The presence of any free methanol formed in this way can be accurately detected by use of Denigès' method.[4] When the above test was applied to mesquite gum it was negative for the glucosidic methoxy but positive for the ether methoxy group. However, all the salts formed by partial hydrolysis of mesquite gum gave positive tests for both the glucosidic and ether methoxy groups. As a check on the accuracy of the method for distinguishing between the two types of methoxy groups when applied to methylated sugars, a sample of tetramethylglucose[5] was tested. This sample showed the presence of both glucosidic and ether methoxy groups. It thus appears that while von Fellenberg's method is suitable for distinguishing between the two types of union in the natural products for which it was devised, it cannot be used to distinguish between the two types of union in the methylated sugars.

The linkage of the methoxy group in mesquite gum seems more stable than a glucosidic linkage could be. This is shown by the following facts. Mesquite gum was hydrolyzed at 100° for twenty-six hours in 3% sulfuric acid solution. The salts obtained from this hydrolysis were further hydrolyzed in 3% sulfuric acid in the autoclave at fourteen pounds' pressure for seven hours. The liquid in which this last hydrolysis was carried out showed only a trace of methanol and the salts obtained after neutralization gave a very strong test for methanol, showing that very little methanol had been removed during the hydrolysis. It was also found that oxidizing the

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[3] T. von Fellenberg, *Biochem. Z.*, 85, 44 (1918).

[4] M. G. Denigès, Compt. rend., 150, 529 (1910).

[5] We are indebted to Dr. F. W. Upson of the University of Nebraska for the sample. It melted at 85° and boiled at 153–156° under 0.2-mm. pressure.

salts with nitric acid of specific gravity 1.15 did not remove the methoxy group to any appreciable extent. It thus appears that the methoxy group is present in mesquite gum as an ether.

The Position of the Methoxy Group in the Organic Acid Occurring in Mesquite Gum.—The approximate position of the methoxy group in the molecule was determined by studying the methoxy content of the various hydrolytic products of mesquite gum. If the gum is hydrolyzed at 80° for six hours, all of the arabinose is removed. Crystalline E-arabinose can be obtained quantitatively, and as the salt formed at the same time contains galactose, a uronic acid and a methoxy group, the methoxy is not attached to the arabinose. If this salt is hydrolyzed further, pure crystalline galactose can be obtained as well as a salt containing only a trace of galactose, a uronic acid and the methoxy group. Therefore, the methoxy is not attached to the galactose but is attached to the uronic acid. Nothing definite can be said as to which carbon atom in the uronic acid this methoxy group is joined, except that it cannot be to carbon atom one or six, since it is present as an ether, not as a glucosidic group.

The Identification of *d*-Glucuronic Acid.—The presence of *d*-galacturonic acid or d-glucuronic acid in the free condition in a mixture can be established by oxidizing the uronic acid with bromine and obtaining mucic acid or saccharic acid, both of which can be identified. In mesquite gum, however, no simple uronic acid is present but a stable methoxyuronic acid. The gum must be hydrolyzed and the methoxy group removed if the uronic acid is to be identified by conversion to mucic or saccharic acid. Numerous unsuccessful attempts were made to identify mucic or saccharic acid among the products by hydrolyzing mesquite gum and oxidizing the resulting mixture with bromine. Finally some calcium salts obtained by hydrolyzing the gum first in the boiling water-bath and then in the autoclave were freed from sugars by dissolving in water and precipitating with alcohol. These salts were converted to the free acid by treatment with sulfuric acid and the acid was purified by dissolving in alcohol. Approximately 30 g. of this acid was placed in an evaporating dish with 200 cc. of nitric acid, specific gravity **1.15,** and the solution concentrated on the water-bath to a gum. This gum was dissolved in water and again concentrated. The acids were neutralized with calcium carbonate, the mixture heated and the calcium oxalate filtered off from the hot solution. The calcium in the filtrate was precipitated by addition of potassium carbonate, filtered and the solution made acid with glacial acetic acid, filtered and concentrated on the water-bath to a small volume. After standing in the refrigerator for some days, the crystals were filtered off and recrystallized from water and acetic acid. They appeared to be identical with potassium acid saccharate crystals made from glucose and with the crystals pictured in van der Haar.[6] The percentage of potassium was determined by conversion to potassium sulfate.

Anal. Calcd. for $KHC_6H_8O_8$: K. 15.75. Found: K, **15.89, 15.81.**

By the above method approximately 1 g. of pure recrystallized potassium acid saccharate was obtained. Since this work was repeated on *a* later occasion, it is certain that d-glucuronic acid is present. **A** strong positive

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[6] A. W. van der Haar, "Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydsauren," Gebrüder Borntraeger, Berlin, 1920, p. 120.

test for methanol was obtained on the mother liquor from which the potassium acid saccharate separated out, showing that the methoxy group was interfering with the formation of the saccharic acid.

The Analytical Methods Used and the Value of the Various Determinations.—Since the methods used in the analysis of the gums are often inaccurate, a brief summary will be given of the determinations that were made and the value that should be attached to each before discussing the quantitative results of this work.

The substances were analyzed for calcium oxide as ash, carbon dioxide evolved by the d-glucuronic acid, free aldehyde, d-galactose, *l*-arabinose, methanol, carbon and hydrogen.

All samples, except those used for the carbon and hydrogen determinations, were dried to constant weight in *vacuo* over phosphorus pentoxide using an Abderhalden vacuum drier and a bath of boiling toluene. The samples for the carbon and hydrogen determinations were dried to constant weight in *vacuo* over phosphorus pentoxide at 85°.

The percentages of calcium oxide reported as ash in this article are slightly high. This is a logical result of the method used in the preparation of the salts, which was to add calcium carbonate to a water solution of sulfuric acid and the organic acid, filter off the calcium sulfate and precipitate the calcium salt of the organic acid by addition of alcohol. It is difficult under these conditions to free the salt completely from calcium sulfate even by repeatedly dissolving in water and precipitating by alcohol. A trace of calcium sulfate in the salt increases considerably the percentage of ash without seriously affecting the other determinations.

The naphthoresorcinol test[7] was used as a qualitative test for a hexose uronic acid, while the carbon dioxide method of Lefèvre[8] as given by van der Haar was followed in the quantitative determination of the uronic acid. This is an accurate method and the results are reliable.[8c,d]

The method employed for determining the free aldehyde group was that of Cajori,[9] using an alkaline iodine solution as the oxidizing agent. The percentage of free aldehyde found by this method in the calcium salts of the monobasic acids was slightly less than the theoretical. This may in part be due to a slight oxidation of the aldehyde group of the salts during their formation.

The free acid of which mesquite gum is a salt, as well as the dibasic acids formed by oxidizing the aldehyde group of the monobasic acids with barium hypoiodite, all absorbed some iodine although they should have no free aldehyde group. This is easily explained. The free acid was prepared by

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[7] C. A. Browne, "Handbook of Sugar Analysis," John Wiey and Sons, Inc., New York, 1912, p. 393; J. A. Mandel and C. Neuberg, *Biochem.* Z., 13, 148 (1908); B. Tollens, *Ber.*, 41, 1788 (1908); B. Tollens and F. Rorive, *ibid.*, 41, 1783 (1908).

[8] (a) A. W. van der Haar, Ref. 6, p. 71; (b) C. G. Schwalbe and G. A. Feldtmann, *Ber.*, 58,1534 (1925); (c) W. H. Dore, THIS JOURNAL, 48,232 (1926); (d) A. D. Dickson, H. Otterson and K. P. Link, *ibid.*, 52, 775 (1930); (e) J. R. Bowman and R. B. McKinnis, *ibid.*, 52, 1209 (1930).

[9] F. A. Cajori, *J. Biol. Chem.*, 54, 617 (1922).

treating mesquite gum in water solution with cold hydrochloric acid, precipitating the product with alcohol. If in this process an occasional molecule was partly hydrolyzed, the product would absorb iodine and thus show a small percentage of free aldehyde. Also if during the oxidation of the monobasic acids with barium hypoiodite insufficient time were allowed for the completion of the process, the resulting acids would show a small amount of aldehyde.

The percentages of d-galactose were determined by the mucic acid method, following as closely as possible the directions of van der Haar.[10] The results were in all cases low. It is now generally recognized that this determination should not be classed as a quantitative process.[11] When the method is applied to gums and pectins the results are often very inaccurate. In one case von Fellenberg reports[1'] 54.8% galactose where the calculated is 75.6%. It seems that the accuracy of the determination depends largely on the nature of the linkage in the molecule. In the case of gum arabic the last molecule of galactose is easily removed[12] and in this case the galactose can be accurately determined.[13] On the other hand, the last molecule of d-galactose is very difficult to remove from mesquite gum and in this case the method yields lower percentages than the theoretical.

The percentage of arabinose was determined by mixing the sample with 12% hydrochloric acid, distilling off the furfural and precipitating it as the phloroglucide.[14] The directions given in the "Official Methods of Analysis" were followed. The results obtained on the free organic acid were about 2% lower than the theoretical. All of the other substances analyzed gave from 3 to 7% arabinose by this method, though no arabinose was actually present. This method is known to be only approximately quantitative. The yield of furfural from arabinose is not quantitative and the amount varies with different operators.[15] Furthermore, the furfural is contaminated with products that vitiate the results. Hexoses give hydroxymethylfurfural, which precipitates along with the furfural.[16] In addition hexose uronic acids yield furfural under the conditions of the determination and the yield is less than the theoretical.[8d] In the case of d-glucuronic acid an accurate factor has been worked out for correcting the

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[10] A. W. van der Haar, Ref. 6, p. 125.

[11] F. Ehrlich, *Chem.-Ztg.*, **41**, 197 (1917); T. von Fellenberg, *Biochem. Z.*, **85**, 118 (1918).

[12] F. Weinmann, *Ber.*, 62, 1637 (1929).

[13] C. L. Butler and L. H. Cretcher, THIS JOURNAL, 51, 1519 (1929).

[14] "Official Methods of Analysis of the Association of Official Agricultural Chemists," Washington, D. C., 1924, 2d ed., p. 120; A. W. van der Haar, Ref. 6, p. 61.

[15] N. C. Pervier and R. A. Gortner, *Ind. Eng. Chem.*, **15**, 1167, 1255 (1923).

[16] R. A. Gortner, "Outlines of Biochemistry," John Wiley and Sons, 1929, p. 525; A. G. Norman, *Biochem. J.*, 23, 524 (1929).

weight of the furfural phloroglucide for the furfural evolved by the hexose uronic acid.[17] No such factor is known for methoxyglucuronic acid. It is obvious that the accuracy of this determination is not great.

The presence of the methoxy group was determined qualitatively by means of the Denigès test for methanol.[3,4] The amount of methoxy was determined quantitatively by the Zeisel method.[18] The percentage found in all the monobasic acids checked the theoretical very closely. In the case of the dibasic acids formed by oxidizing the monobasic acids with an alkaline solution of barium hypoiodite, the percentages of methoxy were slightly low. This is easily accounted for by the fact that an alkaline solution seems to remove traces of methoxy from the methylated sugars.

The percentages of carbon and hydrogen were determined by Dr. E. Yusa at the University of Vienna and checked satisfactorily.

Attempts were made to determine the molecular weight of the free acid from mesquite gum by the cryoscopic method. However, no constant freezing point could be obtained. Since the substance is a free acid, its minimum molecular weight was determined by titrating with sodium hydroxide solution

Preparation and Analysis of the Free Acid of Mesquite Gum.—The method used by Ehrlich in preparing pectic acid[19] was found to work satisfactorily in preparing and purifying the free acid of mesquite gum: 300 g. of mesquite gum was dissolved in 600 cc. of water, filtered, 60 cc. of concentrated hydrochloric acid added and the gum precipitated by addition of 15 liters of 85% ethanol. This precipitate was dissolved in 300 cc. of water and 40 cc. of concentrated hydrochloric acid diluted with 40 cc. of water added. The precipitate was again dissolved and thrown down by addition of 5.5 liters of 88% ethanol. This process was repeated five times. The gum was then dissolved in 250 cc. of water and 1350 cc. of 95% ethanol added to precipitate a small amount of gum and thus eliminate any metallic salts that might be present. The solution was centrifuged and the clear solution poured into a large volume of 95% ethanol. The precipitated material was allowed to settle, triturated with a pestle, filtered, washed with absolute alcohol and ether. The free organic acid finally obtained was a white amorphous powder which was practically free from ash, completely free from chlorides and readily soluble in water. A 0.008 N solution showed a P_H of 3.4. Table I gives the results of the analysis of this acid. The figures obtained check very closely the values calculated for a compound consisting of one molecule of methoxyglucuronic acid joined to three molecules of d-galactose and four molecules of *l*-arabinose with the loss of seven molecules of water.

Partial Hydrolysis of Mesquite Gum to Digalactoso and Trigalactoso Methoxy-*d*-glucuronic Acids.—When mesquite gum was hydrolyzed at 80° with 3% sulfuric acid, all the *l*-arabinose and part of the d-galactose were removed. The resulting solution was

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[17] F. Ehrlich and F. Schubert, *Biochem.* Z., 169, 65 (1926).

[18] H. Meyer, "Analyse und Konstitutionsermittlung organischer Verbindungen," J. Springer, Berlin, 1916, p. 739; E. S. Ripping and W. H. Perkin, "Organic Chemistry," W. and R. Chambers, London, 1909, p. 498; O. Kamm, "Qualitative Organic Analysis," John Wiley and Sons, 1923, p. 172; J. T. Hewitt and T. S. Moore, *J. Chem. Soc.*, 81, 318 (1901); W. H. Perkin, *ibid.*, 83, 1367 (1903).

[19] F. Ehrlich, *Z. angew. Chem.*, 40, 1305 (1927).

neutralized with calcium carbonate, the calcium sulfate filtered off and the calcium salts precipitated by pouring into alcohol. These crude salts were separated by the method of Levene[20] into five fractions, all of which were analyzed. The most soluble and least soluble portions corresponded to definite compounds. The details of this experiment are given below.

Four kilos of mesquite gum was hydrolyzed in 500-g. lots as follows.

Five hundred grams of mesquite gum was dissolved in **3** liters of distilled water, strained through a fine piece of cheese cloth, **60** cc. of concentrated sulfuric acid added (making approximately a **3%** sulfuric acid solution) and the flask immersed in a water-bath at 80° and heated for eleven hours. The solution was neutralized with calcium carbonate, filtered and concentrated on a large evaporating dish over boiling water in the presence of an excess of calcium carbonate. When the volume was about **500** cc., it was filtered with suction and the filtrate poured into a large volume of **95%** ethanol and left to stand overnight to settle. The alcohol was poured off, the thick sirupy material stirred with fresh 95% ethanol, and then extracted twice for one hour each time with boiling ethanol. The thick, gummy residue was dissolved in enough water so that a fine flocculent precipitate was obtained on pouring it slowly into a large volume of 95% ethanol to precipitate the salts. The gummy residue was extracted twice for two hours with hot 95% ethanol and dissolved in water, heated in the boiling water-bath with norit, filtered and precipitated by pouring into a large volume of 95% ethanol; **744** g. of air-dried, dark brown salts was obtained from the **4** kg. of gum. These dark brown salts were purified as follows: **100** g. of salts was dissolved in **750** cc. of water and then **150** cc. of **6** N sulfuric acid and **150** g. of norit (previously boiled with 6 *N* sulfuric acid and washed with water) were added. The mixture was heated rapidly and boiled for one minute, cooled under the tap and filtered. The filtrate was neutralized with calcium carbonate, filtered and the filtrate concentrated by vacuum distillation in a water-bath at 80°, filtered again and the salts precipitated by pouring into a large volume of 95% ethanol. This treatment gave a white salt. The total yield from the 744 g. of crude salts was **423** g.

This salt was separated by fractional precipitation as follows. It was dissolved in three times its weight of water (**400** g. of salt dissolved in **1200** cc. of water). This solution was filtered through a double filter paper to remove the calcium sulfate. After standing overnight and being filtered again, **2400** cc. of **95%** ethanol (two times the

TABLE I

ANALYTICAL DATA AND PHYSICAL CONSTANTS

	Methoxyglucuronic +3 galactoses +4 arabinoses $-7H_2O$. Free acid of mesquite gum		(Methoxyglucuronic +3 galactoses $-3H_2O$-H)$_2$Ca salt 1		(Methoxy-glucuronic +galactoses $-2H_2O$-H)$_2$Ca salt 2		(Methoxy-glucuronic +1 galactose $-H_2O$-H)$_2$Ca salt 3	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
Molecular weight	1222	1222	.....	1426	.....	1102	...	778
Specific rotation	+70.8°	.....	+16.8°	.....	+38 5°	.....	...	....
Ash, %	0.07	0.0	4.31	3.93	5.34	5.08	7.46	7.20
Carbon dioxide, %	3.55	360	6.24	6.17	7.91	7.99	10.00	11.31
Free aldehyde, %	0.48	0.0	2.40	4.07	5 04	5.26	6.99	7.46
Galactose, %	26.77	44.2	59.74	75.73	48.79	6533	23.90	46.27
Arabinose, %	47.02	49.1	5.03	0.0	7.17	0.0	2.91	0.0
Methoxy, %	2.86	2.54	3.90	4.35	5.78	5.63	...	....
Carbon, %	45.46	44.2	41.94	42.07	41.34	41.38	...	....
Hydrogen, %	6.39	6.06	8.09	5.75	6.12	5.63	...	....

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[20] P. A. Levene and H. Sobotka, J. *Biol. Chem.*, 71, 471 (1927); W. F. Goebel, *ibid.*, 72, 813 (1927).

volume of water) was added. It was left to stand overnight, thus allowing the gummy matter to separate out, and in the morning the clear supernatant liquid was decanted and concentrated in vacuum. From this solution the calcium salt was precipitated as described before and 67 g. of this most soluble salt was obtained. The gummy residue was dissolved in 535 cc. of water, 1070 cc. of 95% ethanol added and the liquid centrifuged to hasten the separation of the liquid and residue. In this way five different fractions were precipitated. The final residue gave the least soluble salt (96 g.). All the fractions were analyzed, but the most soluble and least soluble were the only fractions that were pure compounds. The analyses of these two compounds are given in Table I. The least soluble salt (Salt 1) is the calcium salt of methoxyglucuronic acid joined to three molecules of galactose with the loss of three molecules of water. The most soluble salt (Salt 2) is the calcium salt of the methoxyglucuronic acid joined to two molecules of galactose with the loss of two molecules of water.

Oxidation of Digalactoso and Trigalactoso Methoxyglucuronic Acids to Dibasic Acids.—The calcium salts of digalactoso and trigalactoso methoxy-d-glucuronic acids (Salts 1 and 2) were oxidized by barium hypoiodite solution[21] and the resulting dibasic acids isolated as the calcium salts in the form of a white amorphous powder. These salts gave the naphthoresorcinol test and on treatment with 12% hydrochloric acid gave carbon dioxide, thus proving the presence of a hexose uronic acid. This fact proves that the free aldehyde group in the digalactoso and trigalactoso methoxyglucuronic acids was on the galactose and not on the uronic acid. The dibasic salt 1A obtained by oxidation of the monobasic salt (1) is the calcium salt of one molecule of methoxyglucuronic acid joined to two molecules of galactose and one molecule of galactonic acid with the loss of three molecules of water. The dibasic salt 2A obtained by the oxidation of the monobasic salt (2) is the calcium salt of one molecule of methoxyglucuronic acid joined to one molecule of galactose and one molecule of galactonic acid with the loss of two molecules of water. The analyses of these salts are given in Table II.

TABLE II

ANALYSES OF SALTS

	(Methoxyglucuronic + 2 galactose + 1 galactonic − 3 H_2O-2H)Ca salt (1A)		(Methoxyglucuronic + 1 galactose + 1 galactonic − 2 H_2O-2H)Ca salt (2A)	
	Found	Calcd.	Found	Calcd.
Molecular weight	....	748	.....	586
Specific rotation	+2.7°	....	+12.8°	....
Ash, %	6.53	7.49	9.74	9 55
Carbon dioxide, %	6.21	5.88	8.06	7.51
Free aldehyde, %	0.34	0.00	0.23	0.00
Galactose, %	57.28	72.19	46.30	61.43
Arabinose, %	5.35	0.00	5.11	0.00
Methoxy, %	3.40	4.14	4.75	5.29
Carbon, %	40.48	40.11	38.10	38 91
Hydrogen, %	5.89	5.35	5.27	5.12

Partial Hydrolysis of Mesquite Gum to Monogalactoso Methoxyglucuronic Acid.—When mesquite gum is hydrolyzed for a longer time than when preparing the digalactoso and trigalactoso methoxyglucuronic acids, the monogalactoso methoxyglucuronic acid can be obtained. The following procedure was used. One kilo of mesquite gum was hydrolyzed in 500-gram lots as follows: 500 g. of mesquite gum was dissolved in 3

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[21] W. F. Goebel, *J. Biol. Chem.*, 72, 809 (1927).

liters of water and 60 cc. of concentrated sulfuric acid dissolved in 200 cc. of water added. This solution was hydrolyzed in a water-bath at 85° for twenty hours. It was neutralized with calcium carbonate, treated with norit, filtered and the filtrate concentrated in vacuum, using paraffin to prevent foaming, until the liquid had a refractive index of 1.38. The salt was reprecipitated by pouring into a large volume of ethanol and worked up as described under the preparation of the other salts. It was dissolved in 250 cc. of hot water, filtered and precipitated again by pouring into a large volume of ethanol. One kilo of gum gave practically 300 g. of salt. This 300 g. of salt was dissolved in water, 57 cc. of concentrated sulfuric acid added and the solution diluted to 1800 cc. It was heated in a water-bath at 80 to 85° for fourteen hours, neutralized with calcium carbonate, heated with norit, filtered and the filtrate concentrated in vacuum. The salt was precipitated from this solution by pouring into a large volume of alcohol; the yield of salt was about 200 g. This salt was separated by fractional precipitation, It was dissolved in 300 cc. of water, 600 cc. of 95% ethanol added and the liquid concentrated, etc., giving the most soluble salt. The gummy residue was dissolved in 225 cc. of water and some salt precipitated by addition of 450 cc. of 95% ethanol. This process was repeated four times, when the gummy residue was worked up giving the least soluble portion of the salts.

All the fractions were analyzed and the least soluble portion was found to be a fairly pure sample of the calcium salt of methoxyglucuronic acid joined to one molecule of galactose with the loss of one molecule of water. The analysis for this salt (Salt 3) is given in Table I.

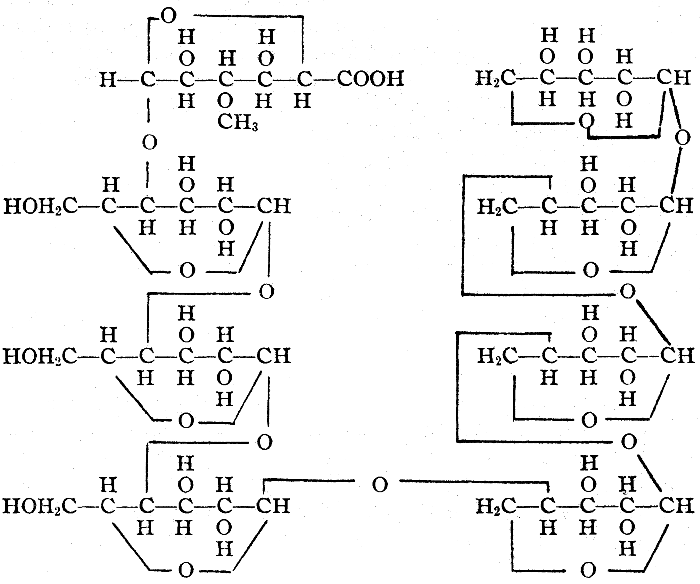
The Structure of Mesquite Gum.—From the work reported above certain facts can be deduced in regard to the structure of the complex organic acid occurring in mesquite gum.

The arabinose must be joined to the molecule by some kind of loose union, since it can be removed completely when the gum is hydrolyzed for six hours with 3% sulfuric acid at 80°. As the free gum does not reduce Fehling's solution, there must be either a dicarbonyl union involving at least one molecule of arabinose or a glucosidic union between the aldehyde of the end arabinose and some hydroxyl in the molecule. Since the compounds of the uronic acid with one, two or three molecules of galactose reduce Fehling's solution, there are only four possible positions for a dicarbonyl union—between the first and second, second and third, third and fourth molecules of arabinose or between the fourth molecule of arabinose and the first molecule of galactose. As immediately upon hydrolysis the molecule begins to reduce Fehling's solution, it seems logical to assume that the dicarbonyl union is between the first two molecules of arabinose, but as no compounds containing part of the arabinose attached to the molecule could be obtained, this position could not be proved. If, however, it is a glucosidic linkage, it could be between the aldehyde group of the first arabinose and any of the numerous hydroxyl groups in the molecule.

On the other hand, the galactoses are quite firmly attached in the molecule. As the different degradation products contain only one free aldehyde group and as one after another of the galactose molecules can be removed by hydrolysis, it seems as if these molecules must be joined together in a chain by means of glucosidic linkages with a free aldehyde group on the end galactose molecule. To which hydroxyl of the sugar the aldehyde is joined is mere conjecture. As in many polysaccharides the aldehyde is joined to the hydroxyl of the fourth carbon atom, this is likely to be the case here. Whatever this linkage is, it can be broken when the gum is hydrolyzed at 80° with 3% sulfuric acid.

As was pointed out when considering the dibasic acids, there is conclusive evidence that the linkage between the galactose and the uronic acid is through the aldehyde

group of the acid and an hydroxyl of the sugar. Methylation studies will be necessary to prove which atom of the galactose is involved in this union. The structure given in the diagram summarizes the results of this study of the acid occurring in mesquite gum.



Tentative structural formula of the complex organic acid occurring in mesquite gum.

Summary

Mesquite gum is the inorganic salt of an organic acid consisting of four molecules of arabinose, three molecules of galactose and one molecule of methoxyglucuronic acid united with the loss of seven molecules of water. This pure acid was prepared and its composition substantiated by preparation of three degradation products: (1) the calcium salt of methoxyglucuronic acid joined to three molecules of galactose with the loss of three molecules of water, (2) the calcium salt of methoxyglucuronic acid joined to two molecules of galactose with the loss of two molecules of water, (3) the calcium salt of methoxyglucuronic acid joined to one molecule of galactose with the loss of one molecule of water. The composition of Salts 1 and 2 was further verified by oxidizing them and obtaining: (1A) the calcium salt of methoxyglucuronic acid joined to two molecules of galactose and one molecule of galactonic acid with the loss of three molecules of water, (2A) the calcium salt of methoxyglucuronic acid joined to one molecule of galactose and one molecule of galactonic acid with the loss of two molecules of water.

Work is now in progress on the methylation of mesquite gum.

TUCSON, ARIZONA

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

THE STEREOCHEMICAL STUDY OF DIPHENYL 2,2'-DISULFONIC ACID. VIII[1]

By W. M. Stanley and Roger Adams

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The existence of optical isomers in substituted diphenyl compounds is, according to the obstacle theory, due to the fact that the ortho-substituted groups are sufficiently large to prevent free rotation. In a previous paper[2] it was shown that x-ray data on the sizes of atoms and groups of atoms may be used to calculate the relative interferences of the ortho substituents and thus to predict whether or not a compound might possibly be resolved. It was pointed out also that the values for each group should not be regarded as representing merely linear effects since the forces around an atom or group are certainly three dimensional in character. The interference values for certain definite molecules were designed to represent the interference due to the effective realms of influence of the various combinations of atoms or groups. Some confusion regarding the interpretation of the obstacle theory appears to exist, since Bergmann[3] suggests the obstacle theory is unnecessary and yet considers the "mutual influence of the electron shells of the atoms or groups" to be the chief consideration. The influence of the electron shells, in so far as they affect the size of the atom or group by causing it to have a larger or smaller realm of force or influence, has been an integral part of the obstacle theory as far as the interpretation in this Laboratory is concerned. By the size of the atom or group is simply meant the volume affected by the electrical forces of the atom, and it is this volume of force that is regarded as the obstacle. The volume of the electrical forces of the atom or group has dimensions and occupies space so that a second volume of force may not be superimposed upon or pass through the first, although the two volumes may approach each other closely. Hence the field of force of the first acts as an obstacle to the field of force of the second atom or group which may strive to pass through or occupy the same space. This is recognized as a simple mechanical interference and the term "obstacle theory" appears quite satisfactory for it. This is in contradistinction to the so-called electrical theory, which represents the atoms or groups as possessing residual affinity of either a negative or a positive electrical charge which, in turn, prevents free rotation in the diphenyl molecule. The attraction of ortho-substituted groups of unlike charge and the repulsion of groups similarly charged are thus assumed to

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[1] For the previous paper (VII) in this series see, Maxwell and Adams, This Journal, 52, 2959 (1930).

[2] Stanley and Adams, *ibid.*, 52, 1200 (1930).

[3] Bergmann and Engel, *Z. physik. Chem.*, Abt. B, 8, 111 (1930).

be determined chiefly by the magnitude of such charges, and with no consideration of the size of the groups.

According to the obstacle theory the size of the group or atom, as determined by the fields of force without regard to the sign or amount of any residual affinity, is the determining factor as to whether or not interference occurs and thus makes resolution of such diphenyl compounds possible. It must be recognized that the angle at which substituents are attached to the benzene ring, as well as the angle between two benzene rings, may vary slightly according to the character of the substituents. This must be taken into consideration, as has been pointed out and exemplified in a previous article.[2]

Although diphenyl derivatives having three and four ortho-substituents have been and are the subject of considerable study, only one compound having but two ortho-substituents has been investigated. This compound, diphenic acid, failed to resolve. On the basis of x-ray data, the following possible interferences of the substituents in the 2,2′,6,6′-positions were obtained: C-H, 0.94Å.; C-COOH, 1.56Å.; C-C (2,2′ and 6,6′), 2.9Å. The carboxyl groups would fail to collide with the hydrogen atoms by 0.4Å.; 1.56Å. + 0.94Å. = 2.5Å. − 2.9Å. ⟶ −0.4Å. It is thus seen that resolution would not be expected. However, it should be possible to resolve such an α,α'-disubstituted diphenyl compound into optical isomers, provided the two substituting groups are sufficiently large and provided also that a hydrogen atom may serve as a blocking group. For example, if each of the two substituting groups was 0.4Å. or more larger than a carboxyl group, they would not only collide with each other but should also collide with the hydrogen atoms when the molecule becomes arranged so that the substituting groups are on opposite sides.

In this investigation diphenyl-2,2′-disulfonic acid was prepared in an attempt to secure groups larger than the carboxyl groups. Pauling[4] and Goldschmidt[5] have calculated the ionic radii of the sulfur ion in sulfates as 0.29 and 0.34Å., and the ionic radii of the carbon atom in carbonates as 0.2Å. The C-O distance in a carbonate group has been estimated by means of crystal analysis as 1.08 Å.,[6] the S-O distance in a sulfate group as 1.55Å.,[7] the C-C distance in aromatic compounds as 1.45Å. and the S-S distance in gaseous S_2 as 1.81Å. and as 2.08Å.[8] in Fe_2S. This indicates that the sulfur atom is from 25 to 50% larger than the carbon atom, or from 0.38 to 0.76Å. larger. If other factors do not interfere and the increase in the sulfonic acid group as indicated by the C-O and the S-O dis-

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[4] Pauling, THIS JOURNAL, 49, 765 (1927).

[5] Goldschmidt, *Trans Faraday Soc.*, 25, 253 (1929).

[6] Lennard-Jones, *Proc. Roy. Soc.* (London), A113, 673, 690 (1927).

[7] "Annual Reports," 1926, p. 274.

[8] Mecke, *Z. Physik*, 42, 390 (1927).

tances is effective, the total sulfonic acid group should be more than 0.4Å. larger than the carboxyl group. Interference with the hydrogen atoms would thus be made possible with the subsequent possibility of resolution of the compound. However, it was found impossible to resolve diphenyl-2,2′-disulfonic acid through the di-brucine, di-quinine and di-morphine salts. These salts were fractionated from several different solvents and gave no indication of resolution. An intermediate product, 4,4′-diamino-diphenyl-2,2′-disulfonic acid was also found to be unresolvable in the form of the di-brucine and di-strychnine salts. It would appear, therefore, that the sulfonic acid group may not be sufficiently large to interfere with a hydrogen atom and prevent free rotation. It may have a more compact structure than was supposed or else the hydrogen atom may be smaller as a blocking group than has previously been assumed. The second possibility appears plausible because the hydrogen atom represents a special case, in that it is different from all other substituting groups by not having an electron shell.

Other possible atoms or groups which, substituted in the α,α' positions in diphenyl, might make free rotation impossible are the bromine atom, the iodine atom and certain ring structures. Thus, 2,2′-dibromodiphenyl should be resolvable for the C-Br distance is approximately 2.11Å., which would cause the bromine atoms to interfere with the hydrogen atoms approximately 0.15Å. A 2,2′-di-iododiphenyl, if no abnormality occurs in the iodine atom when substituted in the benzene ring, should also resolve, for the C-I distance is about 2.2Å. This would cause the iodine atoms to interfere with the hydrogen atoms by 0.24Å. Diphenyl compounds having rings as the large disubstituted groups, may also be prepared. These conclusions depend on the validity of the assumption that the hydrogen atom has an appreciable interfering effect (0.94Å.). Representatives of the above type are now under investigation.

The diphenyl-2,2′-disulfonic acid was prepared by the sulfonation of nitrobenzene to *m*-nitrobenzene sulfonic acid, reduction to azobenzene disulfonic acid by means of zinc dust and alkali and further reduction and rearrangement by means of stannous chloride and hydrochloric acid to 4,4′-diaminodiphenyl-2,2′-disulfonic acid. Removal of the two amino groups by diazotization and treatment with copper powder in ethyl alcohol gave diphenyl-2,2′-disulfonic acid. Several attempts to prepare the disulfonic acid by reducing m-nitrobenzene sulfonic acid in alkaline solution to the hydrazo compound and filtering rapidly into concentrated hydrochloric acid to cause rearrangement to 4,4′-diaminodiphenyl-2,2′-disulfonic acid resulted in failure.

Experimental Part

***m*-Nitrobenzene Sulfonic Acid.*-**Nitrobenzene sulfonic acid was prepared by the sulfonation of nitrobenzene.[9]

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[9] Holleman, *Rec. trav. chim.*, 24, 198 (1905).

Azobenzene Disulfonic Acid.[10,11]—A mixture of 200 g. of potassium *m*-nitrobenzene sulfonate and 255 g. of sodium hydroxide in 1700 g. of water was heated on a steam cone and 204 g. of powdered zinc was added during six hours. The mixture was filtered hot and washed with hot water. The wash water was combined with the filtrate and saturated with carbon dioxide and then concentrated by evaporation until crystals appeared. After cooling a 40-g. crop of white crystals was removed and the filtrate was concentrated to about one liter. On cooling overnight a crop of 115 g. of yellow crystals of the sodium salt of azobenzene disulfonic acid came out. These were removed by filtration and used without drying in the next step.

4,4′-Diaminodiphenyl-2,2′-disulfonic Acid.[11]—A solution of 80 g. of stannous chloride in 160 cc. of concentrated hydrochloric acid was slowly added to a solution of 115 g. of the sodium salt of azobenzene disulfonic acid in 400 cc. of hot water. Upon addition of the stannous chloride the solution gradually loses its yellow color, finally becomes colorless and then white crystals of 4,4′-diaminodiphenyl-2,2′-disulfonic acid precipitate out. After standing overnight these were removed, dissolved in dilute ammonium hydroxide, filtered from a small amount of insoluble material, and reprecipitated by the addition of hydrochloric acid. The run was repeated and the total yield was 160 g.

Diphenyl-2,2′-disulfonic Acid.[11]—Dilute sodium hydroxide was added to a mixture of 100 g. of 4,4′-diaminodiphenyl-2,2′-disulfonic acid in 1.5 liters of ice water until solution was effected. Then 41 g. of sodium nitrite was added and after solution was complete a cold solution of 120 cc. of concentrated sulfuric acid in 500 cc. of water was slowly added and the clear solution allowed to remain at 0° for three days. During this time long yellow needles crystallized out. These were removed, washed with 100 cc. of cold water and air dried for fifteen minutes. The weight of the partially dried product was 100 g. The product was placed in an 800-cc. beaker, covered with 200 cc. of 95% ethyl alcohol and copper bronze added slowly with stirring. The mixture warmed up and nitrogen was evolved. When the reaction was ended, the mixture was heated on the steam cone for fifteen minutes and filtered from the unreacted copper bronze. The filtrate was concentrated until practically free of alcohol and then taken up in 200 cc. of water. A solution of 80 g. of barium hydroxide in 600 cc. of water was then added and the 800 cc. of solution was filtered hot from a small amount of black insoluble material. On cooling a 50-g. crop of white crystalline barium salt of diphenyl-2,2′-disulfonic acid came out. This precipitate was removed and warmed with 12 g. of concentrated sulfuric acid in 200 cc. of water and filtered from the precipitated barium sulfate. Dilute sulfuric acid was then added dropwise to the filtrate until the addition gave no additional white precipitate of barium sulfate. The precipitated barium sulfate was then removed by filtration and the filtrate evaporated to a thick sirup which solidified on standing over phosphorus pentoxide for two days. Diphenyl-2,2′-disulfonic acid is very soluble in water and alcohol, soluble in acetone, and insoluble in chloroform, benzene and petroleum ether. It is very deliquescent.

Preparation and Fractionation of the Alkaloid Salts

Brucine Salt of Diphenyl-2,2′-disulfonic Acid.—A mixture of 5 g. of diphenyl-2,2′-disulfonic acid and 12.5 g. of brucine was boiled with 100 cc. of water until complete solution was effected. On cooling the salt separated as an oil which solidified after standing for a day. The salt was washed with water and then with 100 cc. of hot benzene. After drying the weight of the salt was 17.5 g. and the melting point was 244–246°. ***Rotation.*** (a) 0.3121 g. made up to 25 cc. in chloroform at 20° gave $\alpha_D = -0.8°$;

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[10] Mahrenholtz and Gilbert, *Ann.*, 202, 332 (1880).

[11] Limpricht, *ibid.*, 261, 327 (1891).

$l = 2$; $[\alpha]^{20}_{\rm D}$ −32.0; (b) 0.3382 g. made up to 15 cc. in chloroform at 20° gave $\alpha_{\rm D}$ = −0.76"; $l = 1$; $[\alpha]^{20}_{\rm D}$ −33.6.

The salt was washed with 50 cc. of acetone, *Rotation.* 0.2413 g. made up to 20 cc. with chloroform at 20° gave $\alpha_{\rm D}$ = 0.38°; $l = 1$; $[\alpha]^{20}_{\rm D}$ −31.6. This product was analyzed after drying over phosphorus pentoxide for an hour at 100° and 10-mm. pressure.

Anal. Calcd. for $C_{58}H_{62}O_{14}N_4S_2$: S, 5.81; neut. equiv., 551.3. Found: S, 5.62; neut. equiv., 548.2.

Petroleum ether was added to a solution of 4 g. of the salt in 50 cc. of chloroform until about half of the salt was precipitated out. The remainder of the salt was obtained by evaporation of the filtrate. Both fractions gave essentially the same rotation and melting point as the original material. A solution of 8 g. of brucine salt in 100 cc. of hot water was allowed to cool to 30° with stirring. A 3.5-g, crop of crystals which separated was removed by filtration. On standing overnight a second crop of 0.85 g. of crystals had separated from the filtrate. These were removed and the filtrate was evaporated to 40 cc. and on cooling a 3.2-g. crop of crystals was obtained. The rotation and melting points of all three fractions were identical. A third portion of di-brucine salt was fractionated by crystallization from 95% ethyl alcohol. Both fractions melted at 245–248° and had a rotation in chloroform of $[\alpha]^{20}_{\rm D}$ −33.2.

Quinine Salt of Diphenyl-2,2′-disulfonic Acid.—A mixture of 5 g. of diphenyl-2,2′-disulfonic acid and 10.3 g. of quinine was boiled with 400 cc. of water without effecting solution. The water was removed by evaporation on a steam cone and the residue was dissolved in 200 cc. of chloroform. The addition of petroleum ether caused a 7.5-g. portion of salt melting at 188–192° to precipitate. *Rotation.* 0.3045 g. made up to 15 cc. with chloroform at 20° gave $\alpha_{\rm D}$ = −1.6′; $l = 1$; $[\alpha]^{20}_{\rm D}$ −78.9.

This salt was washed with 100 cc. of ether and analyzed after drying over phosphorus pentoxide for two hours at 100° and 10-mm. pressure. The melting point was then 191–193" with sintering at 185°. *Rotation.* 0.285 g. made up to 15 cc. with chloroform at 20° gave $\alpha_{\rm D}$ = −1.63′; 1 = 1; $[\alpha]^{20}_{\rm D}$ −85.9.

Anal. Calcd. for $C_{52}H_{58}O_{10}N_4S_2$: S, *6.66;* neut. equiv., 481.3. Found: S, 6.41; neut. equiv., 485.4.

The further addition of petroleum ether caused a 7-g. portion of di-quinine salt melting at 188–193° to precipitate. *Rotation.* 0.2453 g. made up to 15 cc. with chloroform at 20° gave $\alpha_{\rm D}$ = −1.3°; 1 = 1; $[\alpha]^{20}_{\rm D}$ −79.5. *A* solution of the di-quinine salt in 40% ethyl alcohol was fractionated into two fractions of 3.3 and 3.7 g. Both fractions melted at 189–192° and the rotations were −83.5 and −81.2, respectively.

Morphine Salt of Diphenyl-2,2′-disulfonic Acid.—A mixture of 3 g. of diphenyl-2,2′-disulfonic acid and 1.65 g. of morphine was boiled with 75 cc. of water until complete solution was effected. The solution was cooled and filtered from 0.01 g. of insoluble material and further evaporated. The salt was so soluble that it was impossible to fractionate it from water, so the aqueous solution was evaporated to a sirup. This sirup was dissolved in 150 cc. of hot ethyl alcohol. On cooling the solution a 0.75-g. portion of salt came out. This fraction of salt began to swell at 240° and melted at 260–265" with decomposition. *Rotation.* 0.1513 g. made up to 15 cc. with water at 20" gave an = −0.73; 1 = 1; $[\alpha]^{20}_{\rm D}$ −72.5.

The filtrate was evaporated to 75 cc. and a 0.5-g. portion of salt came out on cooling. This fraction began to swell at 240° and melted at 261–267° with decomposition. *Rotation.* 0.2237 g, made up to 15 cc. with water at 20° gave $\alpha_{\rm D}$ = −1.11; 1 = 1; $[\alpha]^{20}_{\rm D}$ −74.6.

The filtrate was evaporated to dryness and gave 1.65 g. of salt, which began to swell at 240° and melted at 261–267° with decomposition. *Rotation.* 0.1952 g. made up to 15 cc. with water at 20° gave $\alpha_{\rm D}$ = −0.98; $l = 1$; $[\alpha]^{20}_{\rm D}$ −75.1.

Anal. Calcd. for $C_{46}H_{48}O_{12}N_2S_2$: neut. equiv., **442.** Found: 441.

The di-morphine salt was insoluble in chloroform, benzene, petroleum ether, ethyl acetate and acetone. The salt was also insoluble in absolute ethyl alcohol, but after moistening the salt with a small amount of water it dissolved in ethyl alcohol quite readily.

Strychnine Salt of 4,4′-Diaminodiphenyl-2,2′-disulfonic Acid.—A mixture of 5 g. of 4,4′-diaminodiphenyl-2,2′-disulfonic acid and 9.7 g. of strychnine was boiled for a half hour with 250 cc. of water. On cooling a 7.4-g. crop of salt melting at 310–318° (dec.) was obtained. *Rotation.* 0.2207 g. made up to 15 cc. with water at 20° gave $\alpha_D = -0.33$; $l = 1$; $[\alpha]^{20}_D$ −22.4.

Anal. Calcd. for $C_{54}H_{56}O_{10}N_6S_2$: Neut. equiv., 506.2. Found: 513.

The filtrate was evaporated to 120 cc. and on cooling 2 3 g. of salt was obtained. The filtrate was then evaporated to dryness, giving 3.3 g. of salt melting at 310–318° with decomposition. *Rotation.* 0.3060 g. made up to 15 cc. with water at 20° gave $\alpha_D = -0.43$; $l = 1$; $[\alpha]^{20}_D$ −21.4.

Brucine Salt of 4,4′-Diaminodiphenyl-2,2′-disulfonic Acid.—A mixture of 5 g. of 4,4′-diaminodiphenyl-2,2′-disulfonic acid and 11.4 g. of brucine was gently boiled for a half hour with 250 cc. of water. On cooling a 7.5-g. crop of dibrucine salt melting at 310–313° (dec.) was obtained. *Rotation.* 0 2715 g. made up to 15 cc. with water at 20° gave $\alpha_D = -0.38$; $l = 1$; $[\alpha]^{20}_D$ −21.0.

Anal. Calcd. for $C_{58}H_{64}O_{14}N_6S_2$: neut. equiv., 566.2. Found: 576.

The filtrate was evaporated to 190 cc. and on cooling a 5.5-g. crop of salt melting at 311–314° (dec.) was obtained. *Rotation.* 0.3010 g. made up to 25 cc. with water at 20° gave $\alpha_D = -0.24$; $1 = 1$; $[\alpha]^{20}_D$ −20 0.

The filtrate was evaporated to dryness, giving 3 g. of salt melting at 310–314° with decomposition. *Rotation.* 0.3107 g. made up to 15 cc. with water at 20° gave $\alpha_D = -0.52$; $l = 1$; $[\alpha]^{20}_D$ −24.6.

Summary

The di-brucine, di-quinine and di-morphine salts of diphenyl-2,2′-disulfonic acid, and the di-brucine and di-strychnine salts of 4,4′-diaminodiphenyl-2,2′-disulfonic acid have been prepared. Fractionation of these salts from several different solvents gave no indication of resolution.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF TULANE UNIVERSITY]

THE CHEMISTRY OF FURFURAL. THE PREPARATION OF TETRAETHYLDIAMINODIPHENYLFURYLMETHANE HYDROCHLORIDE AND OF DIPHENYLFURYLMETHANE[1]

BY S. A. MAHOOD AND HELEN F. ALDRICH

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Unlike benzaldehyde, furfural does not condense with the hydrogen atoms para to the amino group of two molecules of aniline when furfural and aniline are treated with a dehydrating agent, but condenses with the hydrogens of the amino group. For this reason, in the synthesis of the diphenylfurylmethane dyes, the amino hydrogen atoms must be absent as in the tertiary amines, or protected by the formation of a sulfate or acetyl derivative.

In 1877, at the same time that he made malachite green, Otto Fischer[2] prepared, by the condensation of dimethylaniline and furfural, the first diphenylfurylmethane dye. He described the furyl analog as lighter in color than malachite green and unstable to light. Renshaw and Miss Naylor[3] found it darker than, and as stable as, malachite green.[4]

This paper describes the preparation of tetraethyldiaminodiphenylfurylmethane hydrochloride, from the condensation of diethylaniline and furfural, and the properties of this dye.

From the figures given on the yields in the synthesis of the leuco base of this dye and of the oxidized product, it can be said that in neither case do the reactions involved proceed easily under the conditions maintained. The following conclusions may be added: (1) the replacement of a phenyl group of malachite green by the furyl group causes a change in the stability of the dye; (2) the ease of condensation of an aldehyde with an aromatic amine is decreased when a furyl group is substituted for a phenyl group in the aldehyde; and (3) diethylaniline condenses with furfural less readily than dimethylaniline. There is a possibility that the stability of these dyes might be increased by substitution in the α'-positions of the furan ring.

Mahood and Harris[5] were able to prepare the furan analog of the dye

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[1] Abstract of a thesis presented by Helen F. Aldrich to the faculty of Graduate Studies of Tulane University in partial fulfilment of the requirements for the Degree of Master of Science, June, 1930.

[2] O. Fischer, Ber., 10, 1626 (1877).

[3] Renshaw and Naylor, THIS JOURNAL, 44, 862 (1922).

[4] Samples of silk treated with this dye were found by the authors of this paper to be more unstable to light than samples dyed with malachite green, when exposed to bright daylight for two weeks.

[5] Mahood and Harris, THIS JOURNAL, 46, 2810 (1924).

benzoflavin from m-toluylene-diamine sulfate, refluxed with furfural. Mahood and Fenner,[6] however, were able to isolate, only in minute quantities, any diaminodiphenylfurylmethane formed by the condensation of furfural with acetanilide, while Mahood and Martin[7] were unable to isolate any of the above product from the condensation of furfural with aniline sulfate.

Because diaminodiphenylfurylmethane was not isolated in quantity, the preparation of diphenylfurylmethane directly from the latter by diazotization, according to the method used by Otto Fischer to prove the structure of the triphenylmethane dyes, was impossible. Mahood and Jordan[8] attempted to prepare this compound by several methods. In each case they were unsuccessful, either because under the influence of the heat or reagents necessary the furfural polymerized before taking part in the reaction, or because no product could be isolated.[9]

This paper also describes the preparation of the above product, diphenylfurylmethane, by a synthesis which involves first transforming the furfural to a more stable derivative, pyromucic acid, and then treating the ethyl ester of the latter with phenylmagnesium bromide to obtain diphenylfurylcarbinol, which on reduction with zinc and acetic acid gives the desired product.

The combustion values given in the experimental data agree with the calculated values for diphenylfurylmethane. The temperature of the reduction was kept low to prevent the formation of a fluorene linkage between the two phenyl groups.

Experimental Part

Preparation of **Tetraethyldiaminodiphenylfurylmethane.**—In a 500-cc. flask were placed 61.5 g. of freshly distilled diethylaniline, 18.1 g. of refined furfural and 20 g. of fused zinc chloride, finely pulverized. The flask, connected with a reflux condenser and a mechanical stirrer, was heated on a water-bath for eleven hours. At the end of this time there was still much unchanged diethylaniline, but more prolonged heating did not increase the yield of the product. The somewhat viscous, dark colored reaction mixture was subjected to steam distillation in the same flask, to remove unchanged furfural and diethylaniline. The crystalline leuco base left behind in the flask after steam distillation was washed with water to remove excess zinc chloride, dissolved in alcohol, boiled with boneblack and filtered while hot. Light yellow crystals separated, which darkened on exposure to air. This product, on recrystallization from ligroin, melted

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[6] Mahood and Fenner, "Tulane Theses," 1927, Vol. 2, p. 152.

[7] Mahood and Martin, "Tulane Theses," 1925, Vol. 3, p. 491.

[8] Mahood and Jordan, *Science,* 60, 453 (1924).

[9] Recently, Peters and Fischer [THIS JOURNAL, 52, 2079 (1930)] have isolated impure phenylfurylcarbinol, the product which Jordan failed to isolate, and from which he intended to prepare the corresponding chloride, as a step in the synthesis of diphenylfurylmethane. All efforts to chlorinate this carbinol were found, by Peters and Fischer, to result in the formation of resins.

completely at 78° but softened several degrees below this. *A* yield of *22* g. or 31% was obtained in this way.

Anal. Calcd. for $C_{25}H_{32}N_2O$: N, *7.45*. Found: *N, 6.82, 6.91.*

Preparation of **Tetraethyldiaminodiphenylfurylmethane** Hydrochloride.—Following the proportions given by **Gattermann**[10] for the oxidation of the leuco base of malachite green, the product obtained above was oxidized in acid solution with lead peroxide paste. The oxidation was carried on for two hours in the cold, accompanied by mechanical stirring. After elimination of the lead salts, the dye was precipitated as the double zinc chloride salt by means of a saturated solution of sodium chloride. *A* yield of 17.2% was obtained.

This dye is crystalline and dark green in color. It dyes silk a yellower color than malachite green, and, in the lighter tones, gives a clear bright green. Dyed samples were fast to washing, but faded somewhat on two week's exposure to bright light, whereas samples dyed with malachite green were unaffected.

Preparation **of Diphenylfurylcarbinol.**—Phenylmagnesium bromide was prepared according to **Gilman,**[11] from 10 g. of magnesium and *76* g. of phenyl bromide, in the presence of *200* cc. of ether. When the reaction was complete, *75* cc. of toluene was added and the ether distilled off; *19.6* g. of ethyl pyromucate,[12] prepared from pyromucic acid,[13] was dissolved in 25 cc. of toluene and added to the Grignard reagent with sufficient rapidity to cause vigorous refluxing. The temperature maintained was about *112°*.

When the reaction was complete, the cooled mixture was decomposed with ice to which the theoretical amount of 30% acetic acid had been added. The toluene layer was separated. After removal of the toluene and diphenyl by steam distillation, a crystalline mass of a light brown color was left behind. This residue was only slightly soluble in cold ligroin and could be recrystallized from this medium in the form of beautiful, light colored, rhombic crystals, melting at *91°* (corr.).[14] Fine white crystals of the same melting point could also be obtained by precipitation from a dilute solution in 87% ethyl alcohol, on the slow addition of water. After standing for a few days, these crystals of diphenylfuryl carbinol soften into a reddish mass. An 85% yield of this carbinol was obtained.

Preparation of **Diphenylfurylmethane.**—Three grams of the carbinol obtained above was dissolved in about 150 cc. of glacial acetic acid, in a large glass test-tube; *15* g. of zinc dust was added in small amounts to the solution. During this time the contents of the test-tube were heated in a water-bath, the temperature of which was kept below 70°. When the solution had changed in color from red to a pale yellow brown, it was poured into water and partially neutralized with sodium hydroxide. A spongy yellow precipitate, which hardened on drying, collected in a mass and was ground to a powder, washed until neutral and dried. It melted at 51° (corr.). The zinc residue left in the test-tube was further boiled with acetic acid. In this way more of the precipitate was obtained. The product was unstable, softening in a few days to a gummy mass. It was soluble in alcohol, ether, ligroin and hot glacial acetic acid. The yield was 95% of the theoretical, calculated as diphenylfurylmethane.

Anal. Calcd. for $C_{17}H_{14}O$: C, *87.14;* H, *6.02.* Found: C, *87.23, 86.83;* H, *5.77, 5.81.*

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[10] L. Gattermann, "The Practical Methods of Organic Chemistry," translated by Schober and Babasinian, The Macmillan Co., New York, 1921, page *355.*

[11] H. Gilman, THIS JOURNAL, *51,1576 (1929).*

[12] *J.* Malaguti, *Ann., 25, 276 (1838).*

[13] "Organic Syntheses," John Wiley and Sons, Inc., New York, *1926,* Vol. VI, p. *44.*

[14] Hale, McNally and Pater, Am. *Chem.* J., *35, 68 (1906).* These authors prepared this carbinol by a method essentially similar. They give 92.4° as its melting point.

Summary

1. A new dye, tetraethyldiaminodiphenylfurylmethane hydrochloride, has been prepared and its properties have been determined.

2. The parent compound of the diphenylfurylmethane dyes, diphenylfurylmethane, has been obtained by reduction of the corresponding carbinol.

NEW ORLEANS, LOUISIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE DISTILLATION OF GRIGNARD REAGENTS

BY HENRY GILMAN AND ROBERT E. BROWN

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Introduction

Solutions of Grignard reagents are mixtures of $RMgX$, R_2Mg, MgX_2, $R—$ and $—MgX$ (or $MgX_2 + Mg$) in a series of equilibria. The following equilibria and dissociation reactions[1] account for the compounds just mentioned.

$$2\ RMgX \rightleftarrows R_2Mg + MgX_2 \qquad (I)$$

$$RMgX \rightleftarrows R— + —MgX \qquad (II)$$

In order to lend additional support to these reactions, studies have been made on the sublimation and distillation of organomagnesium compounds. First, in an attempted high vacuum distillation of methylmagnesium chloride, a distillate or sublimate of magnesium dimethyl, free of halogen, was obtained.'" The magnesium dimethyl, a solid like magnesium diethyl,[3] owes its formation undoubtedly to a displacement of the equilibrium pictured in Reaction I. Second, a search was made for a liquid organomagnesium compound in order to facilitate a study of Reaction I. The relative stability of the liquid beryllium di-*n*-butyl,[4] suggested that greater success might be had with magnesium di-n-butyl. Accordingly, magnesium di-n-butyl was prepared,[2b] but unfortunately it also is a solid. Like its homologs, magnesium dimethyl and magnesium diethyl, it can also be sublimed in a high vacuum but less smoothly than the lower members of this series because of its lesser volatility or lesser stability at elevated temperatures or for both of these reasons.

With this partial success, we turned to a method of distillation used earlier[4] in a study of organoberyllium compounds, namely, ether distillation. This method, which was highly successful for the distillation of solid

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[1] Gilman and Fothergill, THIS JOURNAL, 51, 3149 (1929). This article contains leading references to other work.

[2] (a) Gilman and Brown, *Rec. trav. chim.*, *48*, 1133 (1929); (b) Gilman and Brown, *ibid.*, 49, 724 (1930).

[3] Gilman and Schulze, THIS JOURNAL, 49, 2328 (1927).

[4] Gilman and Schulze, *J. Chem. Soc.*, 2663 (1927). See also, Gilman and Schulze, THIS JOURNAL, 49, 2904 (1927), for organoberyllium halides.

beryllium dimethyl, was found applicable to the magnesium dialkyls, which are, however, distinctly less volatile than the related beryllium dialkyls. After having demonstrated that magnesium dialkyls can be distilled by this procedure (see Experimental Part), a study was made of the ether distillation of RMgX compounds. When alkylmagnesium halides were treated in this manner, the distillate was found to contain the alkylmagnesium halide. Unfortunately, however, this does not prove that the RMgX compound as such distilled over. This is so because we have shown that under the conditions of our distillation magnesium halide or its etherate also distils. Accordingly we are in no position as yet to state whether the RMgX compound contained in the distillate was due to the separate distillations of R_2Mg and of MgX_2 (see Reaction I), each of which is known to distil, or to the distillation of these two compounds *and* some of the RMgX as such.

If equimolecular parts of R_2Mg and of MgX_2 distilled, then the ratio of Mg:X in the distillate should be one. In two analyses of a distillation of methylmagnesium iodide, the ratio Mg:I was found to be 1.105 and 1.092, respectively. These results merely indicate that almost equimolecular parts of R_2Mg and MgI_2 distil, but they do not tell us whether any RMgI distilled. Even though the ratio agreed with the theoretical for Mg:I, we would still have no compelling evidence of the distillation of RMgX as such. Apart from our primary objective, the results are interesting in showing that RMgX or its ***equivalent*** ($R_2Mg + MgX_2$) does distil, because a combination of $R_2Mg + MgX_2$ reacts immediately[1] to give RMgX. It may be possible to find a more definite answer with solvents other than ether.

Apparently arylmagnesium halides cannot be distilled in this manner. At least, when phenylmagnesium bromide was used no magnesium diphenyl and no magnesium bromide distilled during the eighteen consecutive full days of distillation. Just why the magnesium bromide which we know to be present in solutions of phenylmagnesium bromide was held back, we do not at present know. From the distillation of this Grignard reagent there was isolated some diphenyl. This indicates that with RMgX compounds of this type it may be possible to remove[6] the radical R– or its coupling or disproportionation product (see Reaction II).

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[5] Experiments with this in view are in progress with RMgX compounds like benzohydrylmagnesium chloride, $(C_6H_5)_2CHMgCl$. See Gilman and Zoellner, THIS JOURNAL, 52, 3984 (1930). Benzohydrylmagnesium chloride and related types. like triphenylmethylmagnesium chloride,' convert benzophenone to benzopinacol (studies by K. E. Marple).

It may prove possible to prepare some R_2Mg compounds from Grignard reagents by distilling off the MgX_2 and leaving the R_2Mg behind. However, an apparently more general and satisfactory method for the preparation of R_2Mg compounds directly from Grignard reagents is that of Schlenk and Schlenk, Ber., 62, 920 (1929), wherein 1.4-dioxane is used.

Experimental Part

Apparatus.—The apparatus is shown in Fig. 1. It was constructed entirely of glass, and the long neck above the flask A (of about 150 cc. content) was indented to produce good fractionation and to prevent mechanically entrained particles from reaching the receiver B. A ring seal with a sharp edge was also sealed into the upper part of the neck of flask A to prevent any material from creeping out of A. The trap below the water condenser insured a flow of ether and other volatile substances in one direction only. It was found necessary to have the system sealed with a mercury test-tube seal because pressure was gradually built up in the system.[6]

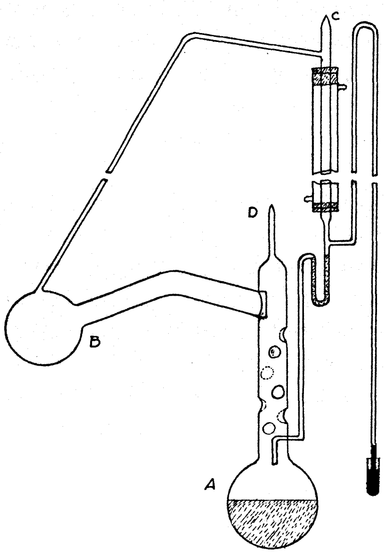

Fig. 1.

The manipulation and operation of the system is as follows. With the tubes C and D open, the apparatus is first thoroughly swept out with dry nitrogen. A solution of the Grignard reagent or MgR_2 compound or MgX_2 compound was then carefully filtered through glass wool into tube C, while the nitrogen continued to flow through D. Tubes C and D were then sealed off. An oil-bath was placed under flask A and the bath was maintained at a temperature of 75–80° by a hot-plate during the course of the experiment. In cool weather a second hot-plate was placed under flask B to drive the ether over into the water condenser and to prevent an undue accumulation of ether in flask B. In warm weather sufficient heat radiated from the plate under A to keep the system in good balance and so make unnecessary a hot-plate under flask B.

At the termination of the experiment, the heating of A was discontinued and the two tubes leading to receiving flask B were sealed off. The smaller of these tubes was next opened to a source of nitrogen, and the contents of B were then investigated. With this apparatus[7] we have found no evidence of creeping, and mechanical entrainment has apparently been annulled. Evidence in support of this is found in the experiment with phenylmagnesium bromide wherein it was shown that the distillate contained neither halogen nor magnesium.

Tests and Analyses.—The R_2Mg and RMgX compounds were tested qualitatively

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[6] Gilman and St. John, *Bull. soc. chim.*, **45**, 1091 (1929), have shown that several typical Grignard reagents can be refluxed at moderately elevated temperatures for several days without any essential impairment in yield of product from the RMgX compound. Possibly the unusually long refluxing used in the present studies may result in a gradual decomposition of the ether or the rate of decomposition of RMgX compound over very long periods may be significant or both of these factors may be involved in the building up of pressure in the system.

[7] This apparatus has some essential improvements over that used in the beryllium dialkyl studies.' It is possible to use a simpler type of apparatus for the ether distillation of other organometallic compounds such as zinc dialkyls which, incidentally, can be prepared in satisfactory yields by the reaction between zinc halides and Grignard reagents.

by the color test[8] and quantitatively by the acid titration[9] method of analysis. They were further characterized by the preparation of α-naphthalides as derivatives.[10]

Time Required and Quantities of Distillate in Ether Distillation.—In the ether distillation experiments with magnesium bromide, magnesium iodide, magnesium diethyl, methylmagnesium iodide, ethylmagnesium bromide, ethylmagnesium iodide and phenylmagnesium bromide about 0.1 mole of compound was used in 75-100 cc. of ether.

With methylmagnesium iodide there was slight evidence of distillate (after distilling ether from receiver B) in about one week from the start of distillation. With ethylmagnesium bromide and iodide there was no evidence of distillate until about the tenth day. Each distillation was run for eighteen full days, and the distillation when once started required practically no attention. This time was arbitrarily selected because it gave a quantity of distillate which though quite small could nevertheless be analyzed. Duplicate distillations were made with practically every compound investigated.

The acid titration of one distillate from methylmagnesium iodide indicated approximately 0.15 g. of distillate calculated as methylmagnesium iodide. The distillates from ethylmagnesium bromide and iodide were not titrated, but they appeared to be somewhat smaller. In the phenylmagnesium bromide experiments the quantity of diphenyl isolated in each distillation was about 0.2 g. Its identity was confirmed by mixed melting point determinations with an authentic specimen.

The apparently inordinate time required for the ether distillation of appreciable quantities of compounds can probably be reduced by the use of other solvents or combinations of solvents.

High Vacuum Sublimation.--The technique used for the high vacuum sublimation was that described earlier. Of the three magnesium dialkyls which were sublimed in a high vacuum, magnesium dimethyl was most volatile. Magnesium di-n-butyl was less volatile than magnesium diethyl. The same order applies to the relative thermal stability of these compounds, magnesium dimethyl being most stable. A free flame was used in the distillation of the magnesium dialkyls, and methylmagnesium chloride was heated in an oil-bath. We have also shown that it is possible to sublime magnesium acetylacetone in a high vacuum.

Summary

In connection with studies on the following systems present in solutions of Grignard reagents

$$2\mathrm{RMgX} \rightleftarrows \mathrm{R_2Mg} + \mathrm{MgX_2}, \text{ and}$$
$$\mathrm{RMgX} \rightleftarrows \mathrm{R}{-} + {-}\mathrm{MgX}$$

it has been shown that some RMgX compounds, or their equivalents, can be distilled in a stream of ether. The high vacuum sublimation of RMgX compounds gives R_2Mg compounds.

AMES, IOWA

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[8] Gilman, Sweeney and Heck. THIS JOURNAL, 52, 1604 (1930). This article contains leading references to earlier studies on the color test.

[9] Gilman, Wilkinson, Fishel and Meyers, *ibid.*, 45, 150 (1923); also Gilman, Zoellner and Dickey, *ibid.*, 51, 1576 (1929).

[10] Gilman and Furry, *ibid.*, 50, 1214 (1928).

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

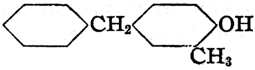
ACTION OF AROMATIC ALCOHOLS ON AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE. V. BENZYLATION OF ORTHO-CRESOL

BY R. C. HUSTON, H. A. SWARTOUT AND GLADYS K. WARDWELL

RECEIVED JULY 24, 1930 PUBLISHED NOVEMBER 5, 1930

In September, 1923, an investigation was started in this Laboratory on the condensation of benzyl alcohol and *o*-cresol in the presence of aluminum chloride. The main product of the reaction crystallized as hard flattened needles which melted at 49.5–50.5° and gave analytical results which indicated a formula of $C_{14}H_{14}O$.

Holleman's amplification of the Beilstein rule[1] would predict that the entering benzyl group would take a position ortho or para to the phenolic hydroxyl. In order definitely to prove this, the compound was heated in a closed tube with $Zn(NH_3)Cl_2$. The resulting amine was diazotized and reduced to the hydrocarbon, which was finally oxidized to *m*-benzoylbenzoic acid.

Our work with the condensation of primary and secondary aromatic alcohols with phenol,[2] as well as the work of Rennie,[3] Gattermann[4] and others with similar reactions, led us to assume that the product containing the benzyl group in the para position to the phenolic hydroxyl would predominate and we tentatively assigned the formula 

. Final proof of this structure was found in the preparation of the isomeric 1-methyl-6-benzylphenol by the Claisen method, as described later in this article.

We were able to isolate from the petroleum ether mother liquor from which the 2-methyl-4-benzylphenol was crystallized a small amount of crystalline material which came down in bundles of very fine needles with a soft silky sheen. A melting point determination gave the rather surprising results of 49.5–50.5°.

A higher-boiling fraction of the reaction product came over after repeated fractionation at 225–227° (5 mm.) as a yellow oil from which we were unable to obtain crystals. Analysis gave results indicating a dibenzyl derivative of o-cresol, $C_{21}H_{20}O$. Because of the powerful directing influence of the phenolic hydroxyl and the behavior of the compound toward strong alkali, we have called it 2-methyl-4,6-dibenzylphenol.

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[1] Holleman, *Chem. Rev.*, 1, 187 (1924).

[2] Huston, THIS JOURNAL, 46, 2775 (1924); 49, 1366 (1927).

[3] Rennie, J. Chem. *Soc.*, 41, 37 (1882).

[4] Gattermann, Ber., 22, 1129 (1889); 23, 1199 (1890).

Upon application of the Claisen[5] method of benzylation to *o*-cresol, we obtained a good yield of a benzylated derivative which was identical in melting point, boiling point, solubility and crystal appearance with the compound which we obtained from the mother liquors of the main product of the aluminum chloride condensation. Besides the 2 methyl-6-benzylphenol, the Claisen process gave a smaller amount of 2 methylphenyl benzyl ether. The o-methyl group of the cresol precluded the formation of *a* di-*o*-dibenzyl derivative.

A short time after the experiment just described had been completed, Schorigin[6] published a description of the benzylation of *o*-cresol by the Claisen method. He stated that 2-methyl-6-benzylphenol melted at 51–52" and boiled at 182–188° (15 mm.).

A comparison of the physical properties of the two monobenzyl derivatives (both of which melt at 49.5–50.5°) brings out some rather striking differences, aside from the difference in appearance of the crystals.

2-Methyl-4-benzylphenol dissolves readily in the calculated amount of dilute potassium hydroxide (5%), is soluble in eighty-seven parts of petroleum ether (40–60°) at 20° and boils at 167–169° (5 mm.).

2-Methyl-6-benzylphenol is insoluble even in a large excess of dilute potassium hydroxide (5%). It dissolves when warmed in the equivalent amount of strong potassium hydroxide (50%), but separates out when an equal volume of water is added. It is soluble in 18.2 parts of petroleum ether at 20°. Its boiling point is seventeen degrees lower than that of its isomer.

The monobromo derivatives of the two monobenzyl cresols were prepared by treating them in chloroform solutions with the calculated amounts of bromine. In the case of 2-methyl-4-benzylphenol we assumed that the bromine entered the phenolic ring in the only available ortho or para position with the formation of 6-bromo-2-methyl-4-benzylphenol.

Making the same assumption, 2-methyl-6-benzylphenol would give 4-bromo-2-methyl-6-benzylphenol. In this last case we were able to prove the validity of the assumption by benzylating 2-methyl-4-bromophenol by the Claisen method to obtain the same product that was formed by the bromination of 2-methyl-6-benzylphenol. This gives additional proof of the structure of the last-named compound.

The two monobenzyl derivatives were further characterized by the preparation of their benzoyl derivatives. It is worthy of note that the 2-methyl-6-benzylphenol in which both ortho positions are occupied reacted much less readily under the Schotten–Baumann treatment than did the isomeric 2-methyl-4-benzylphenol.

The following is a graphic outline of the field covered.

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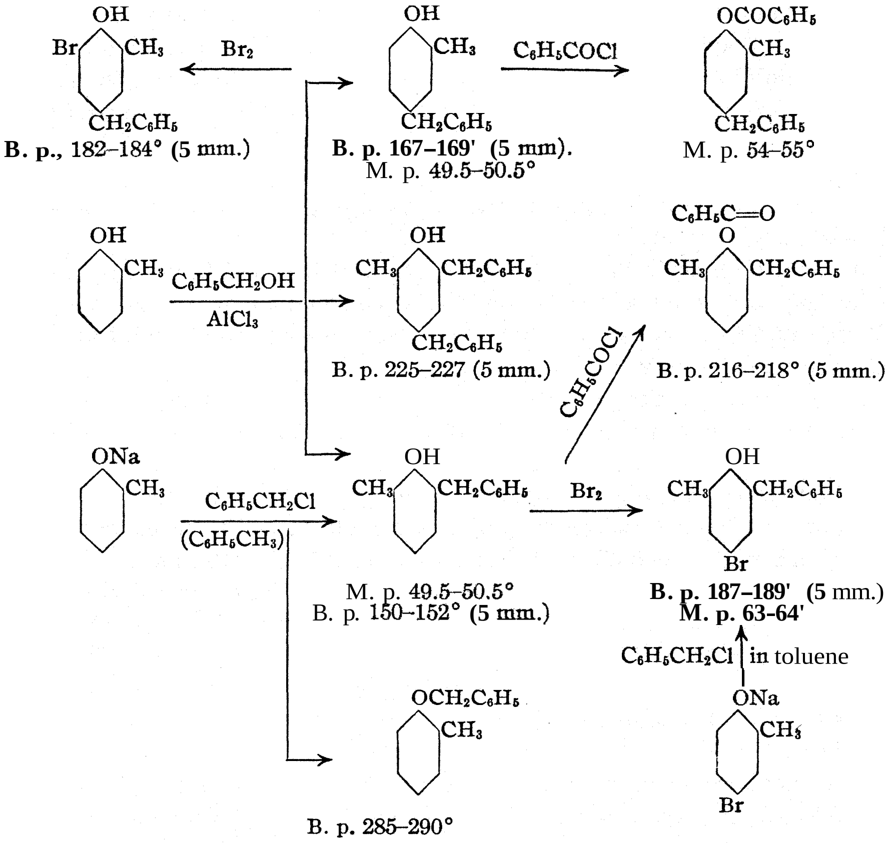
[5] Claisen, *Ann.*, 442, 221 (1924).

[6] Schorigin, *Ber.*, 58B, 2033 (1925).



Experimental

Benzyl Alcohol and o-Cresol with Aluminum Chloride.—A mixture of 100 g. of o-cresol, 100 g. of benzyl alcohol and 200 g. of petroleum ether (40–60°) was placed in a tall vessel, surrounded by water and stirred mechanically while 65 g. of anhydrous aluminum chloride was added in small portions over a period of an hour. The temperature was maintained at 30–35°. At times troublesome frothing occurred which was controlled by the addition of further portions of cold petroleum ether. When the evolution of hydrogen chloride had nearly ceased, the mixture was allowed to stand overnight. The brown semi-solid intermediate product was decomposed with ice and a little hydrochloric acid and extracted with ether. The ether extract was dried over potassium carbonate, the ether distilled off and the residue fractionated under reduced pressure.

Fifth fractionation (5 mm.)

90–150°	12.2 g.
150–170°	51.5 g.
170–215°	3.3 g.
215–235°	26.2 g.
Residue	13.5 g.

The first fraction was crude *o*-cresol.

The second fraction (150–170°) crystallized. The crystals were pressed between filter papers and recrystallized repeatedly from petroleum ether. The purified compound melted at 49.5–50.5° and boiled at 167–169^{e} (5 mm.). It crystallized in clusters or rosets of fine brittle needles. Two 50-cc. portions of a solution of purified crystals in petroleum ether (40–60°) at 20° gave on evaporation 0.5715 g. and 0.5743 g. of residue.

Anal. Subs., 0.523: CO_2, 0.4746; H_2O, 0.0971. Calcd. for $C_{14}H_{14}O$: C, 84.8; H, 7.12. Found: C, 84.99; H, 7.19.

The filter papers which were used to remove the oily impurity from these crystals were extracted with ether and the ether extract was distilled. Two and one-half grams came over at 150–155° (5 mm.). This crystallized when seeded with 2-methyl-6-benzylphenol (see p. 4488) and was further identified by bromination and by its benzoyl derivative.

The 215–235" fraction was repeatedly distilled until most of it came over at 225–227° (5 mm.). All attempts to induce this oil to solidify failed. It is insoluble in dilute potassium hydroxide. In hot 50% potassium hydroxide it changed to a blue, gummy mass, but did not dissolve. Its ready solution in Claisen's alcoholic potassium hydroxide proved it to be a phenol. Its failure to absorb bromine readily when dissolved in chloroform indicated that all positions ortho and para to the phenolic hydroxyl were occupied and justified the assignment of the structure 2-methyl-4,6-dibenzylphenol.

Anal. Subs., 0.2147: CO_2, 0.6861; H_2O, 0.1343. Calcd. for $C_{20}H_{21}O$: C, 87.45; H, 7.00. Found: C, 87.62; H. 7.01.

4-Amino-3-methyl-diphenylmethane.—The phenol which formed the bulk of the 150 to 170° fraction (b. p. 167–169°) was mixed thoroughly in a mortar with twice its weight of zinc ammonia chloride and one-fifth its weight of ammonium chloride. The mixture was sealed in Carius tubes (care being taken not to fill each tube more than one-quarter full) and heated in a bomb furnace for twenty hours at 330".

The reaction product was thoroughly shaken with hydrochloric acid (1:1), allowed to stand overnight and extracted with ether to remove the unchanged phenol. The acid solution was just neutralized with ammonium hydroxide and then treated with dilute sodium hydroxide to precipitate the amine. This came down as very fine light brown plates and was not further purified. Five grams was obtained from 50 g. of phenol.

Preparation of 3-Methyldiphenylmethane and m-Benzoylbenzoic Acid.—Five grams of 4-amino-3-methyldiphenylmethane was dissolved in 15 g. of hydrochloric acid (sp. gr. 1.2) and diluted with 30 cc. of water, Sodium nitrite was added (in 10% solution) until a positive test for nitrous acid was obtained with starch–iodide paper. The solution of diazonium chloride was added slowly to a well-cooled solution of 10 g. of sodium hydroxide in 30 cc. of water and reduced in the cold with sodium stannite (prepared from 20 g. of stannous chloride). Extraction with ether gave 0.6 g. of 3-methyldiphenylmethane boiling at 274–276°.[7] This was oxidized by means of potassium dichromate and sulfuric acid to m-benzoylbenzoic acid melting at 142–144°.[8]

Benzylation of o-Cresol by the Claisen Method.—Twelve grams of sodium was melted under 130 cc. of toluene and shaken to produce "bird-shot" so um. After cooling to room temperature, this was treated with 54 g. of *o*-cresol. The reaction appeared to be complete at the end of two hours, but the mixture was gently heated for another hour under a reflux condenser. The flask was again cooled and 64 g. of benzyl chloride was added. After standing overnight, the mixture was refluxed on an oil-bath for five hours at 150–160°. When cool, the sodium chloride was removed by washing

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[7] Ador and Riiliet, *Ber.*, 12, 2300 (1879).

[8] Senff, *Ann.*. 220, 237 (1883).

twice with water and the toluene was removed by distilling until the temperature reached 125°.

The residue was dissolved in 250 cc. of Claisen's alcoholic potash[9] and shaken out with 200 cc. of petroleum ether (40–60°) in 50-cc. portions. Distillation of the petroleum ether extract gave 16 g. of 2-methylphenylbenzyl ether boiling at 285–290°.[10]

The alcoholic solution left after extraction with petroleum ether was made distinctly acid with hydrochloric acid (1:1), diluted until the potassium chloride first formed was redissolved, and extracted three times with ether. Distillation of the ether left a reddish-brown oil, which was fractionated three times at 5 mm. Seventy-one grams came over at 140–160°, and solidified in the receiver. Repeated recrystallization from petroleum ether gave long white needles or fibers with a soft silky sheen which showed a tendency to form in bundles or a felted mass. The pure compound melted at 49.5–50.5' and boiled at 150–152° (5 mm.) or at 187–189° (15 mm.). This melting point differs from that recorded by Schorigin[11] for 2-methyl-6-benzylphenol by 1.5". Two 50-cc. portions of a solution of the purified crystals in petroleum ether saturated at 20° gave on evaporation 2.7210 g. and 2.7392 g. of residue.

Anal. Subs., 0.1443: CO_2, 0.4473; H_2O, 0.0915. Calcd. for $C_{14}H_{14}O$: C, 84.8; H, 7.2. Found: C, 84.5; H, 7.07.

We were unable to isolate a constant-boiling fraction from the higher-boiling residue.

Bromine Derivatives

6-Bromo-2-methyl-4-benzylphenol was prepared by treating 2-methyl-4-benzylphenol in chloroform solution with a molecular equivalent of bromine at 0°. Evaporation of the chloroform left an oil which distilled at 180–182° (5 mm.). The assignment of structure is based upon the assumption (which has been proved in many cases) that the bromine enters the phenolic ring and upon the directive influence of the hydroxyl group.

Anal. Subs., 0.2582, 0.2071: AgBr, 0.1763, 0.1426. Calcd. for $C_{14}H_{13}OBr$: Br, 28.48. Found: Br, 28.68, 28.87.

4-Bromo-2-methyl-6-benzylphenol was prepared in two ways: (a) by the bromination of 2-methyl-6-benzylphenol in chloroform at 0° and (b) by the benzylation of 4-bromo-2-methylphenol (m. p. 64°) by the Claisen method. It recrystallized from petroleum ether in characteristic rosets. It melted at practically the same temperature as the unbenzylated phenol 63–64', and boiled at 187–189° (5 mm.).

Anal. Subs., 0.2259, 0.2867: AgBr, 0.1550, 0.1961. Calcd. for $C_{14}H_{18}OBr$: Br, 28.48. Found: Br, 28.82, 28.65.

Benzoyl Derivatives

The benzoyl derivative of 2-methyl-4-benzylphenol was readily prepared by the Schotten–Baumann reaction. It crystallized from petroleum ether or alcohol (75%) in small colorless rhombic crystals melting at 54–55°.

The benzoyl derivative of 2-methyl-6-benzylphenol could not be prepared by the Schotten–Baumann reaction because of the insolubility of the phenol in dilute potassium hydroxide. When the latter compound was warmed with an equivalent amount of 50% potassium hydroxide it formed a solution which solidified on cooling. The crude potassium salt was warmed with an equivalent amount of benzoyl chloride. The reaction product was washed with water and distilled. It came over as a very viscous

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[9] Claisen, *Ann.*, 442, 224 (1924).

[10] Staedel, *ibid.*, 217, 45 (1883).

[11] Schorigin, *Ber.*, 58B, 2033 (1925).

light yellow oil at 216–218° (5 mm.). This ester was more readily prepared from the phenol and benzoyl chloride by the pyridine method.

Summary

1. *o*-Cresol was benzylated by means of benzyl alcohol in the presence of aluminum chloride. The main product was 2-methyl-4-benzylphenol. Smaller amounts of 2-methyl-6-benzylphenol and 2-methyl-4,6-dibenzylphenol were formed.
2. Benzylation by the Claisen method gave an excellent yield of 2-methyl-6-benzylphenol.
3. The monobromo derivatives and benzoyl derivatives of the two monobenzylcresols were prepared.

EAST LANSING, MICHIGAN

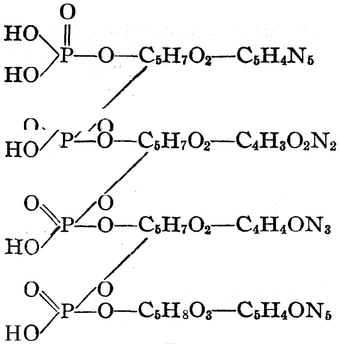
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON PYRIMIDINES. CXVII. A METHOD FOR THE SYNTHESIS OF NUCLEOSIDES

BY G. E. HILBERT[1] AND T. B. JOHNSON

RECEIVED JULY 26, 1930 PUBLISHED NOVEMBER 5, 1930

The present generally accepted structure of a nucleic acid molecule is based chiefly on the results of experimental work by Levene and his coworkers. They represent it as being a tetranucleotide construction, in which the individual nucleotides are combined through phosphoric acid ester linkages as expressed in the formula of yeast nucleic acid I. In this acid the functioning sugar is d-ribose.



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The approach to a synthesis of a nucleic acid molecule calls first for methods of preparation of the pyrimidine and purine nucleosides, which may be considered as the glucosidic constructions characterizing the structure of nucleosides. If one accepts Levene's conception of the constitution of pyrimidine-nucleosides, in support of which he has contributed considerable indirect experimental evidence, the problem of nucleoside synthesis resolves itself into one of finding a practical method of coupling a sugar with a pyrimidine (uracil, thymine or cytosine) at the 3-position of the ring. The purpose of this paper is to describe a method of synthesis which has made it possible to obtain such a glucoside.

A comprehensive study of the behavior of 2,6-dioxy- and 2-thio- or 2-alkyl mercapto-6-oxypyrimidines toward different alkyl halides in alkaline

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[1] Sterling Research Fellow in Chemistry, 1928–1930.

solution by Johnson and his co-workers[2] led to results which did not enable one to formulate definite rules predicting the favorable position of substitution in such alkylation reactions. The active positions were **1** and **3** of the pyrimidine cycle forming nitrogen derivatives, and also the oxygen of the lactam grouping –CONH– forming cyclic imino ethers. Mixtures of mono- and di-substitution products were formed in varying proportions in practically every case examined. Other alkylating agents have also been used. Davidson and Baudisch[3] found that dimethyl sulfate interacted with uracil to form exclusively 1,3-dimethyluracil. Case and Hill[4] employed diazomethane as an alkylating agent, but here also they obtained results quite in accord with the previous observations of Johnson.

That direct alkylation of the pyrimidine and purine cycles is an unsuccessful method for the synthesis of nucleosides has been shown by Fischer[5] and co-workers and more recently by Levene and Sobotka.[6] The same general method was used by all these workers, namely, the action of acetobromoglucose or related combinations on the alkali or silver salts of purines and pyrimidines. The presence of a COMH linkage in both the pyrimidine and purine cycles favored the formation of glucosides which were easily decomposed by hydrolysis. These products were without doubt glucosides in which the sugar was attached to the ring in ether linkage. Fischer was able to obtain glucoside derivatives of purines in which the sugar was attached to the nitrogen of the imidazole ring only in those cases where the enolic isomerization of the cyclic acid amide grouping CO-NH of the ring was excluded, as in the case of theophyllin. Fischer confined his attempts at synthesis chiefly to purine combinations and only **a** few experiments were conducted with pyrimidines.[7] In both cases no products were obtained which resembled the natural nucleosides.

Levene and Sobotka[8] made a rather comprehensive study of the action of

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[2] Johnson and Johns, *Am. Chem.* **J.**, 34, 182 (1905); Johnson and Heyl, *ibid.*, 37, 628 (1907); 38, 237 (1907); Wheeler and Liddle, THIS JOURNAL, 30, 1152 (1908); Johnson and Clapp, **J.** *Biol. Chem.*, 5, 49 (1908); Johnson and Derby, *Am. Chem.* **J.**, 40, 444 (1908); Johnson and Jones, *ibid.*, 40, 538 (1908); Wheeler and Liddle, *ibid.*, 40, 233 (1908); Johnson and Jones, THIS JOURNAL, 31, 590 (1909); Wheeler and Johnson, *Am. Chem. J.*, 42, 30 (1909); Wheeler and McFarland, *ibid.*, 42, 431 and 1011 (1909); 43, 10 (1909); Johnson and Moran, *ibid.*, 48, 307 (1912); Johnson and Zee, *ibid.*, 49,287 (1913); Johnson and Bailey, THIS JOURNAL, 35, 1007 (1913); Johnson and Haggard, *ibid.*, 37, 177 and 2591 (1915); Johnson and Matsuo, *ibid.*, 41, 782 (1919); Johnson and Joyce, *ibid.*, 38, 1385 (1916).

[3] Davidson and Baudisch, THIS JOURNAL, 48, 2379 (1926).

[4] Johnson, Hill and Case, *Proc. Nat. Acad. Sci.*, 8, 44 (1922); Case and Hill, THIS JOURNAL, 52, 1536 (1930).

[5] Fisher and Helferich, *Ber.*, 47,210 (1914); Fischer, *ibid.*, 47,1377 (1914); Fischer and Fodor, *ibid.*, 47, 1058 (1914); Helferich and von Kühlewein, *ibid.*, 53, 17 (1920).

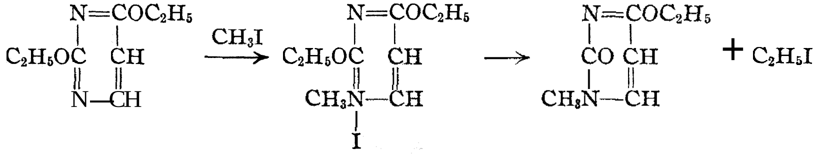
[6] Levene and Sobotka, **J.** *Biol. Chem.*, 65,463,469 (1925).

[7] Fischer, *Ber.*, 47, 1377 (1924).

[8] Levene and Sobotka, **J.** Biol. *Chem.*, 65,469 (1926).

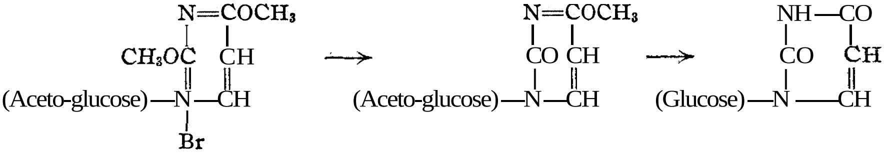
acetobromoxylose on salts of pyrimidines. A great variety of substituents in the pyrimidine cycle were used so as to cover any possible change in reactivity of the molecule. The silver salts of 1-methyluracil, 5-nitrouracil and 2-ethylmercapto-6-oxypyrimidine on treatment with acetobromoxylose led to the formation of oxygen ethers. The silver salt of cytosine did not react. The use of the potassium instead of the silver salts was also unsuccessful. The great difference in behavior toward hydrolytic agents of these synthetic nucleosides and the natural uridine and cytidine was assumed as offering further indirect evidence that the sugar in the pyrimidine nucleosides is linked in the 3-position of the ring.

As a result of the recent work of Hilbert and Johnson,[9] it is now possible to apply a method of alkylation which enables one to control substitution in the 3-position of the pyrimidine ring. This involves the reaction between a 2,6-dialkoxypyrimidine and an alkyl halide which interact in accordance with the equation below, giving a 3-substituted pyrimidine IV. Constructions of this type, IV, easily undergo hydrolysis, giving a normal uracil derivative of known structure.



II III IV

It has now been found that an analogous reaction takes place by treating 2,6-dimethoxypyrimidine with acetobromoglucose, yielding 2-oxy-6-methoxy-3-tetra-acetylglucosido-pyrimidine VI. The intermediate addition product V is unstable at 50°, at which temperature the reaction is carried out. The methyl bromide thus liberated also reacts with 2,6-dimethoxypyrimidine, yielding a large quantity of 2-oxy-3-methyl-6-methoxypyrimidine. The acetylated glucoside VI and 2-oxy-3-methyl-6-methoxypyrimidine were separated by taking advantage of their different solubilities in water, the former being insoluble and the latter very soluble. It was then easily purified by recrystallizing from 50% alcohol, from which it separated in long needles melting at 220–221°.



V VI VII

The 2-oxy-6-methoxy-3-tetra-acetylglucosido-pyrimidine VI was simultaneously de-ethylated and deacetylated on treatment with alcoholic

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[9] Hilbert and Johnson, THIS JOURNAL, 52, 2001 (1930).

hydrochloric acid, yielding 3-glucosido-uracil VII. In its chemical behavior this is similar in every respect to the natural uridine. It is stable toward dilute hydrochloric acid, however, when the double bond is reduced, forming 4,5-dihydro-3-glucosido-uracil; the latter is hydrolyzed with 3% sulfuric acid, yielding glucose and hydrouracil. This remarkable reaction was originally shown to take place by Levene and LaForge[10] with uridine, and the fact that our 3-glucosido-uracil parallels in its stability their findings would seem to be experimental evidence confirming the structure assigned to uridine.

3-Glucosido-uracil was brominated, forming 5-bromo-3-glucosido-uracil, and when acetylated yielded 3-tetra-acetylglucosido-uracil. It also gave a negative Wheeler–Johnson color reaction,[11] as is to be expected with a 3-substituted uracil.

This method for introducing a sugar on nitrogen should also be applicable to other ring systems such as quinolines, pyridines and pyrazolones and also to straight-chain compounds of the imino ether type.

Experimental Part

2-Oxy-6-methoxy-3-tetra-acetylglucosido-pymine—A solution of 2 g. of acetobromoglucose in 2 cc. of 2,6-dimethoxypyrimidine was placed in a stoppered tube and heated at 50° for forty-eight hours. After twenty-four hours the contents of the tube solidified to a colorless crystalline mass. The odor of methyl bromide was noticeable. The reaction mass was triturated three times with 5-cc. portions of water. This water extract on standing deposited colorless needles which were identified as 3-methyluracil;[12] yield, 1 g. The crude acetylated glucoside after treatment with water was usually in the form of a thick paste which solidified upon the addition of 5 cc. of ether. The solid was filtered by suction and thoroughly washed with ether to remove any unchanged acetobromoglucose. It was then recrystallized twice from 50% alcohol, from which it separated as a mass of long needles melting at 220–221° without decomposition; yield, 0.5–0.7 g. (23–32% of the theoretical). 2-Oxy-6-methoxy-3-tetra-acetylglucosido-pyrimidine is sparingly soluble in ether, slightly soluble in hot water, soluble in hot alcohol and very soluble in cold chloroform. The statement made in *Science*[13] that it reduces Fehling's solution after treatment with hydrochloric acid is in error.

Anal. Calcd. for $C_{19}H_{24}O_{11}N_2$: C, 50.00; H, 5.3; N, 6.14. Found: C, 50.60; H, 5.8; N, 6.16.

The influence of the variation of the temperature and of the proportions of the reactants upon the yield of the nucleoside was thoroughly investigated. If the reaction was carried out at room temperature, two weeks were required for completion of the reaction; the yield was 5% of that required by theory. At a temperature of 80° crystallization started within a few hours. However, the yield was only 9%. If equivalent amounts of the reactants were used the yield was not only very poor but the product was also more difficult to obtain pure because of the large preponderance of 3-methyl-

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[10] Levene and LaForge, J. *Biol. Chem.*, 13, 507 (1912–1913).

[11] Wheeler and Johnson, *ibid.*, 3, 183 (1907).

[12] 2-Oxy-6-methoxy-3-methyl-pyrimidine on standing in the aqueous extract is hydrolyzed to 3-methyluracil.

[13] Johnson and Hilbert, *Science*, 69, 579 (1929).

uracil. In large quantity production the reaction was generally smooth. In one case, however, the end-product was partially deacetylated. This on treatment in the appropriate manner with acetic anhydride yielded the desired 2-oxy-6-methoxy-3-tetra-acetylglucosido-uracil.

3-Glucosido-uracil.—A solution of 9 g. of 2-oxy-6-methoxy-3-tetra-acetylglucosido-pyrimidine in 125 cc. of hot absolute methyl alcohol was treated with 30 cc. of a solution of *dry* hydrochloric acid in absolute ethyl alcohol (22% hydrochloric acid by weight). The reaction mixture was allowed to stand at room temperature for twenty-four hours. During this time a solid cake of colorless chunky crystals separated. The product was filtered and after drying weighed 5.6 g. (97% of the theoretical). It was recrystallized from 90% alcohol, from which it separated in the form of hexagons which contained water of crystallization and melted between 195–203°, depending upon the rate of heating. The water of crystallization was very firmly bound and required heating at 115° at 2-mm. pressure for its complete removal.[14] The anhydrous substance melted at 207–209" with decomposition to a milky liquid. Its rotation is $[\alpha]^{23}_{\mathrm{D}} = \$21.4$ in aqueous solution.

Anal. Calcd. for $C_{10}H_{14}O_7N_2(H_2O)_{1/2}$: H_2O, 3.18. Found: H_2O, 3.27, 3.41, 3.48.

Anal. Calcd. for $C_{10}H_{14}O_7N_2$: C, 43.80; H, 5.11; N, 10.22. Found: C, 43.56; H, 5.25; N, 10.12.

3-Glucosido-uracil does not reduce Fehling's solution after boiling with various concentrations of hydrochloric acid for several hours. It also gives a negative Wheeler–Johnson color reaction for pyrimidines of the uracil type.

3-Tetra-acetylglucosido-uracil.—A gram of 3-glucosido-uracil was treated with a solution of 0.5 g. of anhydrous sodium acetate in 10 g. of acetic anhydride and heated on a steam-bath for two hours. The pyrimidine derivative rapidly dissolved, forming a solution with a pale yellow color. On pouring the reaction mixture into 40 cc. of ice water, an oil separated which on standing at 0° slowly crystallized. The solid was filtered, thoroughly washed with water and dried. After treatment with boneblack it was recrystallized twice from 50% alcohol, from which it separated in clusters of prisms; melting point, 154–155°; yield, 1 g.

Anal. Calcd. for $C_{18}H_{22}O_{11}N_2$: N, 6.34. Found: N, 6.33.

5-Bromo-3-glucosido-uracil.—Nine-tenths of a gram of 3-glucosido-uracil was treated with bromine water until the solution had a permanent pale yellow color. The water was removed by distillation under diminished pressure. A pale yellow, sirupy residue remained, which was dissolved in 15 cc. of absolute ethyl alcohol and the resulting solution evaporated to dryness twice in an open vessel with constant stirring. The solid product was recrystallized twice from 90% alcohol, from which it separated as small colorless glistening prisms; yield 1 g. It contained 1% of water of crystallization and melted at 224° with effervescence, turning dark brown. The water of crystallization was very firmly bound and required drying at 115° at 2-mm. pressure for its complete removal. The decomposition point of the anhydrous 5-bromo-3-glucosido-uracil was 238". It was extremely soluble in water and insoluble in organic solvents. The rotation was $[\alpha]^{25°}_{\mathrm{D}} + 10.3°$ in aqueous solution.

Anal. Calcd. for $C_{10}H_{13}O_7N_2Br$: C, 33.99; H, 3.68; N, 7.93. Found: C, 34.18; H, 3.59; N, 8.04.

4-5-Dihydro-3-glucosido-uracil.—A solution of 2 g. of 3-glucosido-uracil in 50 cc. of 80% alcohol was shaken with 0.2 g. of Adams and Shriner[15] platinum oxide catalyst

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[14] Fischer[5,7] found that the water of crystallization in the purine glucosides was also difficult to remove.

[15] Adams and Shriner, Tms JOURNAL, 45, 2171 (1923).

and hydrogen under a pressure of **2-3** atmospheres. Reduction was completed in an hour. The catalyst was removed from the solution and the alcohol distilled under diminished pressure. A colorless sirup remained, which on trituration with absolute alcohol and scratching eventually solidified. The product was recrystallized from **100** cc. of 90% alcohol, yielding 1.2 g. of anhydrous colorless diamond-shaped crystals; 4,5-dihydro-3-glucosido-uracil turns slightly brown at 220° and decomposes at **233°.** It is very soluble in cold water and insoluble in organic solvents. It showed $[\alpha]_D^{24°}$ +9.3° in aqueous solution.

Anal. Calcd. for $C_{10}H_{16}O_7N_2$: C, **43.48; H, 5.80; N, 10.15.** Found: **C, 43.65; H, 5.66; N, 10.19.**

Hydrolysis of **4,5-Dihydro-3-glucosido-uracil with 3% Sulfuric** Acid to **4,5-Di**hydrouracil and Glucose.—One and six-tenths grams of 4,5-dihydro-3-glucosido-uracil was dissolved in 50 cc. of 3% sulfuric acid and refluxed for two hours. The brown colored solution was treated with **8** g. of powdered barium carbonate and heated on a steam-bath until effervescence of carbon dioxide ceased and then finally filtered. The water was removed by distillation under diminished pressure and the crystalline residue dissolved in 5 cc. of boiling water, treated with boneblack and filtered. On cooling, colorless plates of 4,5-dihydrouracil separated; yield, **0.2** g. After recrystallizing from hot water the product melted at 276–277". A mixed melting point with an authentic specimen was unchanged.

'The filtrate from 4,5-dihydrouracil was treated with 0.8 g. of phenylhydrazine hydrochloride and 0.6 g. of sodium acetate and heated on a steam-bath for a few hours. After heating a short time yellow needles of phenylglucosazone started to separate. After recrystallization from dilute alcohol it melted at **207-208".** A mixed melting point with a genuine sample was unchanged.

Conclusion

1. A method for the synthesis of pyrimidine nucleosides has been described. 3-Glucosido-uracil has been prepared by this procedure.

2. 3-Glucosido-uracil is not hydrolyzed by dilute acids, whereas its reduction product, 4,5-dihydro-3-glucosido-uracil, is hydrolyzed by 3% sulfuric acid to hydrouracil and glucose. They thus behave similarly to uridine and its reduction product 4,5-dihydrouridine. This is believed to be the strongest direct experimental evidence yet obtained in favor of the structure of uridine, being 3-ribosido-uracil.

FERTILIZER AND FIXED NITROGEN INVESTIGATIONS
BUREAU OF CHEMISTRY AND SOILS
WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

THE REDUCTION OF PARA-DIMETHYLAMINOBENZIL[1]

BY SANFORD S. JENKINS[2] WITH JOHANNES S. BUCK AND LUCIUS A. BIGELOW

RECEIVED JULY 30, 1930 PUBLISHED NOVEMBER 6, 1930

The work described in this paper is a continuation of that reported in an earlier communication[3] which dealt with the catalytic reduction of a number of symmetrical a-diketones by means of a modified form of the Adams apparatus, using hydrogen under pressure in the presence of a platinum-black platinum oxide catalyst. It seemed desirable to extend this study to include the reduction of the unsymmetrical a-diketone, *p*-dimethylaminobenzil, and this has led to some interesting and not altogether expected results.

The starting material was obtained conveniently by oxidizing *p*-dimethylaminobenzoin, which in turn was prepared in the usual manner by condensing *p*-dimethylaminobenzaldehyde with benzaldehyde in the presence of potassium cyanide according to the method of Staudinger.[4]

Upon reduction by the method already described, the benzil readily took up either one or two molecules of hydrogen, yielding in the one case the corresponding benzoin, and in the other, the analogous p-dimethylaminohydrobenzoin, melting at 112°, which has not previously been reported. It was possible either to isolate the intermediate product, or not, as desired, without affecting the ultimate result.

The hydrobenzoin, on treatment with a mixture of acetic and hydrochloric acids, was readily dehydrated, with the production of *p*-dimethylaminodesoxybenzoin, melting at 128°, and this, on further catalytic reduction, was converted without difficulty into the corresponding *p*-dimethylaminostilbene hydrate, melting at 78°. The hydrate lost a molecule of water in the presence of the acetic–hydrochloric acid mixture, forming the related stilbene, already known,[5] and this on final catalytic reduction yielded, as would be expected, the saturated p-dimethylaminodiphenylethane, which melted at 63°.

Up to this point, the results obtained did not differ in any essential respect from what might have been expected from the earlier work. When, however, an attempt was made to reduce the benzoin with tin and hydrochloric acid in alcohol solution, two isomeric *desoxy* derivatives were obtained, and none whatever of the hydro compound, which is the sole

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[1] This paper is constructed from portions of a thesis presented by Sanford S. Jenkins in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences, Duke University.

[2] Angier B. Duke Memorial Fellow, 1929–1930.

[3] Buck and Jenkins, THIS JOURNAL, 51, 2163 (1929).

[4] Staudinger, *Ber.*, 46, 3537 (1913).

[5] F. and L. Sachs, *ibid.*, 38, 515 (1905).

product of the direct hydrogenation. The existence of these isomers is possible, of course, upon theoretical considerations, but as the benzoin itself gave every evidence of being a single substance, the appearance of the two desoxy compounds at this point was not particularly expected. They are very easily separated, as one is quite soluble in dilute acid while the other is relatively insoluble in this reagent. The first, or *α-p*-dimethylaminodesoxybenzoin melted at 128°, and was identical with the material obtained by catalytic dehydration of the hydro compound, while the other, or *β*-desoxy derivative, melted at 164°.

Each of these substances, upon further reduction with hydrogen, yielded a corresponding stilbene hydrate. The a-derivative, as mentioned above, showed a melting point of 78°, and the *β*-compound, which has been described in the literature,[5] fused at 60°. Both lost water under the influence of the acetic and hydrochloric acid mixture, forming one and the same stilbene, identical with that already described.

A sample of *β-p*-dimethylaminostilbene hydrate was prepared by the Sachs method. It melted at 60°, and when mixed with some of the corresponding material prepared by reducing the desoxy compound, the melting point was not depressed. From this it follows that the structures of the two isomers are as follows

$(CH_3)_2NC_6H_4CH_2CHOHC_6H_5$	$(CH_3)_2NC_6H_4CHOHCH_2C_6H_5$
α-p-Dimethylaminostilbene hydrate, m. p. 78°	*β-p*-Dimethylaminostilbene hydrate, m. p. 60°

Furthermore, the desoxybenzoins from which these compounds are derived by reduction may reasonably be assumed to possess corresponding structures, in which the (CHOH) group is replaced by (CO).

The changes which have been described may conveniently be represented by the diagram.

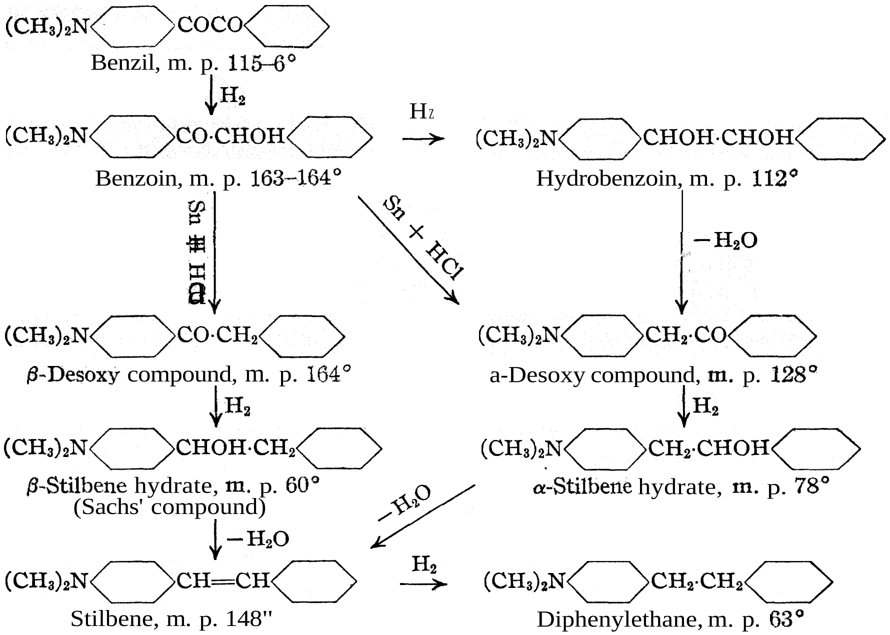
It will be noticed that in this scheme one formula has been assigned arbitrarily to the benzoin, which itself is capable of existing in two isomeric modifications. The reasons for this will be set forth in another paper, which will deal with the structure of this benzoin. It may be stated at this point, however, that while the appearance of two desoxy derivatives made it seem likely that the benzoin itself might be a mixture of isomers, repeated efforts to separate it into a- and *β*-components have not been successful.

Experimental

***p*-Dimethylaminobenzoin.**—This substance was prepared according to the method of Staudinger, already cited. It crystallized in prisms melting at 163–164°.

***p*-Dimethylaminobenzil.**—This compound resulted from the oxidation of the corresponding benzoin with concentrated Fehling's solution as recommended by Staudinger. Ten grams of the benzoin yielded 9.0 g. of benzil (90% of calcd.), which, after crystallization from alcohol, melted at 115–116°.

***p*-Dimethylaminobenzoin by the Catalytic Reduction of the Benzil.**—In this procedure, the modified form of the Adams apparatus, already described, was used. An



THE REDUCTION OF *p*-DIMETHYLAMINOBENZIL

accurate calibration showed that when 0.01 mole of pure benzoin (unsubstituted) took up 0.01 mole of hydrogen, forming hydrobenzoin, the gage showed a drop in pressure of 12 lb. Glacial acetic acid was found, after a number of trials, to be the best solvent. Accordingly, 2.50 g. (0.01 mole) of *p*-dimethylaminobenzil, 0.05 g. of platinum oxide and 50 cc. of glacial acetic acid were placed in the apparatus, and the reduction carried on at room temperature until the requisite drop in pressure was obtained. It should be noted that in mixing the reagents it is best to add the solvent last, to prevent spontaneous ignition of the mixture. After filtering off the catalyst, the solution was diluted with an equal volume of water and the precipitated benzoin filtered and dried. It weighed 1.62 g. (68% of calcd.), and, after one crystallization from alcohol, was obtained as white prisms which melted at 163–164° (corr.). A mixed melting point with a sample prepared by Staudinger's method showed no depression.

***p*-Dimethylaminohydrobenzoin.**—This material was prepared in a manner similar to that described above, except that absolute alcohol proved to be the best solvent, and the reduction was allowed to proceed until the gage registered a drop in pressure of 25 lb., which required about thirty minutes. After removal of the catalyst, the solvent was evaporated under reduced pressure, and the product crystallized twice from ligroin (b. p. 60–70°). Two and one-half grams of the benzil yielded 2.3 g. of the hydro derivative (90% of the theoretical), as snow white prisms, melting at 112° (corr.).

Anal. Calcd. for $C_{16}H_{19}NO_2$: N, 5.44. Found: N (Kjeldahl), 5.44, 5.50.

α-*p*-Dimethylaminodesoxybenzoin. (First Method.)—The a-desoxy compound was formed without difficulty by dehydrating the hydrobenzoin just described. Accordingly, 5.1 g. (0.02 mole) of the substance was heated for twenty minutes with 40 cc. of a mixture of glacial acetic acid and hydrochloric acid. (sp. gr. 1.19) 4:1 by volume. After adding 200 cc. of water, the solution was neutralized with sodium carbonate and the yellow precipitate filtered off and recrystallized from alcohol. The product was obtained in white prisms melting at 128° (corr.), and weighed 3.5 g. which is 70% of the theoretical.

Anal. Calcd. for $C_{16}H_{17}NO$: N, 5.85. Found: N (Kjeldahl), 5.82, 5.95.

β-*p*-Dimethylaminodesoxybenzoin.—It is interesting to note that while this isomer is formed readily in the reduction of the benzoin with tin and hydrochloric acid, not a trace of it appeared in the dehydration of the hydrobenzoin just described. A mixture of 20 g. of *p*-dimethylaminobenzoin, 16 g. of mossy tin, 30 cc. of hydrochloric acid (sp. *gr.* 1.19), 80 cc. of alcohol and 0.5 g. of $CuSO_4 \cdot 5H_2O$ was heated under a reflux condenser for five hours, after which the unchanged tin was filtered off, the solution diluted with 100 cc. of water, and allowed to cool somewhat. After a short time crystals began to form and another 100 cc. of water was added. The mixture was allowed to stand in a cool place for two hours, and the product finally filtered off and recrystallized from alcohol. A yield of 9.0 g. was obtained, which consisted of white or at times cream-colored plates, melting at 164" (corr.). A mixed melting point with the original benzoin, which also melted at 163–164°, showed a large depression.

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.33; H, 7.11; N, 5.85. Found: C, 80.34; H, 7.22; N (Kjeldahl), 5.78.

α-*p*-Dimethylaminodesoxybenzoin. (Second Method.)—The solution from which the β-desoxy compound had been filtered (see above) was made alkaline with sodium carbonate. and a large precipitate obtained. This was separated, washed well with water. sucked as dry as possible and extracted twice with boiling alcohol. The combined extracts were evaporated to a volume of 50 cc. and allowed to cool. The crystals which separated weighed 7.0 g. and, after recrystallization from alcohol, formed white prisms, melting at 128'. A mixed melting point with a sample of the a-desoxybenzoin obtained by the dehydration of the hydro compound showed no depression. The combined yield of the *a*- and β-isomers was 16.0 g., which is 85% of the theoretical.

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.33; H, 7.11; N, 5.85. Found: C, 80.31, 80.55; H, 7.27, 7.36; N (Kjeldahl), 5.92.

a-p-Dimethylaminodesoxybenzoin Oxime.—This compound was prepared by dissolving 2.0 g. of the corresponding desoxybenzoin, and 1.0 g. of hydroxylamine hydrochloride in 10 cc. of pyridine and heating the mixture on the water-bath for three hours. After this, 100 cc. of water was added and the solution allowed to crystallize. The product was filtered, washed with water, dried, and recrystallized from ligroin (b p. 95–98°). It separated in long white needles melting at 139° (con.).

Anal. Calcd. for $C_{16}H_{18}N_2O$: N, 11.02. Found: N (Kjeldahl), 11.00, 11.20.

β-*p*-Dimethylaminodesoxybenzoin Oxime.—This oxime was formed in exactly the same manner as the corresponding a-compound. It separated from alcohol in white prisms melting at 142° (corr.). A mixed melting point with the a-oxime showed a large depression.

Anal. Calcd. for $C_{16}H_{18}N_2O$: N, 11.02. Found: N (Kjeldahl), N, 10.90. 11.02.

a-p-Dimethylaminostilbene Hydrate.—Two and four-tenths grams (0.01 mole) of a-p-dimethylaminodesoxybenzoin, 0.10 g. of platinum oxide and 50 cc. of absolute alcohol were heated to 60° and shaken with hydrogen until the pressure had dropped 13 Ib., which required two hours. The catalyst was filtered off, and the solvent removed under reduced pressure. The crude product was crystallized from ligroin (b. p. 95–98') and separated in long colorless needles, weighing 2.25 g. (93% of calcd.) and melting at 78° (corr.).

Anal. Calcd. for $C_{16}H_{19}NO$: N, 5.80. Found: N (Kjeldahl), 5.79, 5.87.

β-*p*-Dimethylaminostilbene Hydrate. (First Method.)—Considerable difficulty was experienced in the catalytic reduction of β-*p*-dimethylaminodesoxybenzoin, as slight amounts of impurities appeared to inhibit the reaction entirely. However, after repeated crystallization from alcohol, a pure white product was obtained which would reduce slowly. Two and four-tenths grams (0.01 mole) of the desoxy derivative, 0.10 g. of platinum oxide and 100 cc. of absolute alcohol were shaken with hydrogen at 60° for four hours, after which the catalyst was filtered off and the solvent evaporated under reduced pressure. The product crystallized from ligroin (b. p. 95–98°) in clusters of colorless needles weighing 2.10 g. (85% of calcd.) and melting at 60° (corr.).

β-p-Dimethylaminostilbene Hydrate. (Second Method.)—As this stilbene hydrate has been described in the literature, the writers have prepared a sample of it by Sachs' method, already cited, in which *p*-dimethylaminobenzaldehyde is reacted with benzylmagnesium bromide. The product separated in 62% yield from ligroin (b. p. 95–98°) as white needles, melting at 60° (corr.). When the material of known structure was mixed with that prepared by catalytic reduction, the melting point was not depressed.

p-Dimethylaminostilbene.—To prepare this substance, 5.0 g. of *β-p*-dimethylaminostilbene hydrate was heated for twenty minutes with a mixture of glacial acetic acid and hydrochloric acid (sp. gr. 1.19) 4:1 by vol., after which the solution was diluted with 200 cc. of water, neutralized with sodium carbonate and the precipitated product filtered. This was recrystallized from alcohol and separated in colorless scales, weighing 4 g. (90% of calcd.) and melting at 148°. *α-p*-Dimethylaminostilbene hydrate, treated in exactly the same manner, gave an 80% yield of the stilbene, which melted at 148°, and a mixture of the two also fused at 148°.

p-Dimethylaminodiphenylethane.—To prepare this compound, 2.23 g. (0.01 mole) of p-dimethylaminostilbene, 0.05 g. of platinum oxide and 50 cc. of glacial acetic acid were shaken with hydrogen at room temperature for twenty minutes, after which time the pressure had dropped 12 lb. The catalyst was filtered off, the mixture diluted with 200 cc. of water and neutralized with sodium carbonate. The precipitated product was filtered, washed and recrystallized from 60% alcohol. It weighed 1.80 g. (80% of calcd.) and formed nearly white flakes melting at 63° (corr.).

Anal. Calcd. for $C_{16}H_{19}N$: N, 6.22. Found: N (Kjeldahl), 6.35, 6.52.

Addition Product of Methyl Iodide to *p*-Dimethylaminodiphenylethane.—This substance resulted when methyl iodide was added to a solution of *p*-dimethylaminodiphenylethane in absolute ether. The mixture was allowed to stand overnight and the product crystallized out in white plates melting at 260–262° (uncorr.).

Anal. Calcd. for $C_{17}H_{22}NI$: I, 34.6. Found: I (Pringsheim), 34.3.

Summary

1. The complete series of reduction products of *p*-dimethylaminobenzil has been studied.

2. The corresponding benzoin, which seems to be a single substance, yielded the two theoretically possible desoxy derivatives upon reduction under suitable conditions. These compounds in turn can be reduced further to form two isomeric stilbene hydrates. Seven new substances have been prepared and characterized.

Durham, North Carolina

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

THE REDUCTION OF CYSTINE IN LIQUID AMMONIA BY METALLIC SODIUM[1]

BY VINCENT DU VIGNEAUD, L. F. AUDRIETH AND H. S. LORING[2]

RECEIVED JULY 31, 1930 PUBLISHED NOVEMBER 6, 1930

From a consideration of amino acids as ammono compounds it would seem likely indeed that liquid ammonia would be a most suitable solvent for the study of not only these substances, but also of the simple derivatives of the amino acids and possibly for the investigation of the more complex derivatives, the proteins. A study of the solubilities of a number of amino acids in liquid ammonia showed they were quite soluble in most instances. Of particular interest to us was the ready solubility of cystine in this medium, in contrast to its behavior in water. In view of this fact it was decided to investigate the possibility of the reduction of cystine to cysteine, the sulfhydryl form, by means of metallic sodium. It was found that this reaction readily takes place and, in fact, affords an excellent method for the preparation of cysteine.

The general applicability of a solution of sodium in liquid ammonia as a reducing agent has been demonstrated by numerous investigators.[3,4] The experimental procedures outlined below, however, involve the first recorded case which we know of in which reduction of the disulfide linkage to the sulfhydryl group has been effected in this manner.

The slight possibility of a change in cystine itself on treatment with liquid ammonia and subsequent evaporation was eliminated by the quantitative recovery of the cystine having an unchanged rotation. Preliminary reactions were then run to prove that the reduction of the cystine actually leads to the formation of cysteine. Benzylcysteine was obtained in very good yield by adding benzyl chloride directly to the reduced cystine solution in the liquid ammonia. This procedure is the simplest method for the preparation of this derivative of cysteine and should offer a general method for the preparation of similar derivatives. The reduced cystine solution obtained after evaporation of the ammonia and careful neutralization in the cold with acid gave a very strong positive nitroprusside test and a very strong Sullivan reaction.[5] The nitroprusside test was carried out in the usual fashion in aqueous solution but later it was found that the reaction

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[1] A preliminary report of this paper was given before the meeting of the American Society of Biological Chemists in Chicago, March 26–29, 1930.

[2] This communication is an abstract of a thesis submitted by H. S. Loring in partial fulfilment of the requirements for the Degree of Master of Science in Chemistry at the University of Illinois.

[3] Kraus and White, THIS JOURNAL, 45, 768 (1923).

[4] White and Knight, *ibid.*, 45, 1780 (1923).

[5] Sullivan, *Public Health* Repts., U. S. P. H. S., 44, 1599 (1929).

could be carried out directly in the liquid ammonia. Sodium nitroprusside dissolves in liquid ammonia and gives a deep purple-red color with cysteine.

The amount of sodium required for the reduction of the cystine was next investigated. It is well known that sodium dissolved in liquid ammonia. gives a deep blue solution. The disappearance of this blue color was used as the end-point in the reaction with cystine. To a weighed amount of sodium dissolved in liquid ammonia in a liquid ammonia titration apparatus, described by Johnson and Fernelius,[6] cystine was added very slowly until the blue color disappeared. It was found that four atoms of sodium were necessary to reduce one molecule of cystine.

For completeness of reduction probably the best criterion is the optical rotation. Vickery and Leavenworth[7] had come to this same conclusion in their study of the formation of cysteine when cystine is precipitated with silver sulfate. They based their conclusions on the great difference between the rotation of levo cystine and the positive rotation of cysteine obtained from the reduction of levo cystine. Andrews[8] in his study of the reduction of cystine obtained cysteine hydrochloride with a rotation of $+9°$ calculated as cysteine from cystine having a rotation of $-215°$. This positive rotation of cysteine hydrochloride was confirmed by Vickery[7] in the above-mentioned work. Bergmann and Michalis[9] have recently published a method for the preparation of cysteine depending on catalytic reduction with palladium black. These investigators obtained free cysteine, which had a negative rotation of $-10.14°$ in water solution, but a positive rotation of $+6.9°$ in 1 N acid solution. In the present work the rotations of the reduced solutions were followed and found in a great number of runs to have values close to $+7°$. In a number of runs higher values were obtained, in one instance $+12°$.

The method for the preparation of cysteine suggested by the present investigation is particularly simple where the presence of sodium chloride and a trace of ammonium chloride is not undesirable. For the preparation of the free cysteine hydrochloride it is necessary to extract the mixture with alcoholic hydrochloric acid and recrystallize the extracted cysteine hydrochloride from 20% hydrochloric acid. Free cysteine can then be prepared in the usual manner by dissolving the hydrochloride in alcohol and precipitating the cysteine by exactly neutralizing with ammonium hydroxide. The method is particularly advantageous where it is desirable to avoid the introduction of traces of heavier metals in the preparation of cysteine.

Experimental

The liquid ammonia used in the actual preparation of cysteine was obtained from

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[6] Johnson and Fernelius, J. *Chem.* Ed., 6,441 (1929).

[7] Vickery and Leavenworth, J. *Biol. Chem.*, 86, 129 (1930).

[8] Andrews, *ibid.*, 68, 209 (1926).

[9] Bergmann and Michalis, Ber., 63, 987 (1930).

the usual standard laboratory tank. In those experiments in which the molecular ratio of sodium to cystine was determined, the ammonia was dried over metallic sodium in an auxiliary tank, and then passed into the titration apparatus, where it was condensed by means of a bath of solid carbon dioxide in ether.

The cystine was prepared by the method given in "Organic Syntheses,"[10] the samples having specific rotations of −205° to −208°.

Determination of the Molecular Ratio of Sodium to Cystine.—The liquid ammonia titration apparatus[6] used consists of a cylindrical flask 26 cm. long and 3.5 cm. in diameter. A weighing tube is fitted by means of ground-glass connection into a side arm 2 cm. in diameter, located approximately 8 cm. from the top of the apparatus. A second side arm, 7 mm. in diameter, is located opposite the first and contains a stopcock. The flask is closed by means of a ground-glass stopper, through which a 7-mm. tube also containing a stopcock passes to the bottom of the flask.

Approximately 40 cc. of liquid ammonia was condensed into the titration apparatus after all the air had been displaced by first passing ammonia through the flask. A carefully weighed piece of sodium was then quickly added through the side arm of the apparatus; the mixture was stirred by bubbling gaseous ammonia through the solution until the sodium had dissolved. Cystine was then added slowly from the dropping tube, which had previously been weighed. The addition was continued until the blue color due to free sodium had just disappeared. The amount of cystine was then determined by the difference in the weight of the tube before and after the addition of the cystine. The values of the ratios found are given in Table I.

TABLE I

MOLES OF SODIUM NECESSARY TO REDUCE CYSTINE

	Grams	Moles used	Molecular ratio
	Run No. 1		
Wt. of sodium	0.3648	0.01586	4.092
Wt. of cystine	.9302	.003876	1.0
	Run No. 2		
Wt. of sodium	0.185	0.008043	4.179
Wt. of cystine	.462	.001925	1.0

The fact that the amount of sodium used was very slightly higher than the theoretical may be explained by the presence of a small amount of sodium hydroxide, which formed during the weighing, and the transference of the sodium to the reaction flask.

Preparation of Benzylcysteine.—The presence of a sulfhydryl group in the liquid ammonia solution was shown by a positive sodium nitroprusside reaction. To prove the presence of cysteine, benzylcysteine was prepared. An ammonia solution of the reduced cystine as obtained above was allowed to evaporate spontaneously at room temperature. The flask containing the residue was evacuated to remove the last traces of ammonia. A part of the solid remaining was tested for cysteine by the Sullivan reaction,[5] and was found to give a strong positive test. The remainder was treated with benzyl chloride by the method of Gortner and Hoffman[11] for the preparation of benzylcysteine. On acidifying the solution with acetic acid, a large white precipitate formed. This was filtered, washed and recrystallized from boiling water; m. p. 214° (uncorr.); m. p. of benzylcysteine, 213°. This product was soluble in dilute hydrochloric acid and sodium hydroxide and gave a negative nitroprusside reaction.

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[10] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, pp. 39-41.

[11] Gortner and Hoffman, J. *Biol. Chem.*, 72,444 (1927).

Anal. Calcd. for $C_9H_{13}O_2NS$: N, 6.63. Found: N, 6.54, 6.39.

Benzylcysteine in Liquid Ammonia Solution.—Weighed amounts of cystine were reduced with sodium as described above. To the resulting colorless solution the theoretical amount of benzyl chloride (two moles of benzyl chloride for every mole of cystine) was added slowly with stirring. The ammonia solution was evaporated and the sodium salt remaining was dissolved in water and acidified with acetic acid. Benzylcysteine separated out and was purified by recrystallization from hot water; m. p. 212° (uncorr.). Yields of about 70% of the theoretical were obtained.

Anal. Calcd. for $C_9H_{13}O_2NS$: N, 6.63. Found: N, 6.74, 6.88.

Recovery of Cystine from the Reduced Solution.—To determine whether racemization had taken place during reduction, the material obtained after evaporation of the ammonia solution was dissolved in water, neutralized with dilute hydrochloric acid and allowed to stand in contact with air for several days. Cysteine is readily oxidized under these conditions. White particles separated from the solution. Upon recrystallization of this precipitate from dilute acid by the addition of sodium hydroxide, characteristic hexagonal plates of cystine were obtained with an optical rotation of −210°. The optical activity of the original cystine was −208°.

Preparation of Cysteine Solutions and their Optical Activity.—In preparing cysteine solutions for measurements of the optical rotation, it was found that the reaction could be carried out best in a 100-cc. graduated cylinder, cooled in the carbon dioxide–ether cooling bath. A typical procedure consisted in dissolving a weighed amount of sodium, approximately 0.5 g., in about 40 cc. of liquid ammonia, and adding approximately 1 g. of cystine from a weighing bottle, leaving an excess of sodium in the solution. The amount of cystine used was accurately determined. The resulting blue solution, which contained an excess of sodium, was then neutralized by the addition of an amount of ammonium chloride equivalent to the sodium used (1.16 g. for 0.5 g. of sodium). The mixture, which contained sodium chloride and the ammonium salt of cysteine, was evaporated to dryness at room temperature in the absence of air. To remove traces of free ammonia the cylinder was evacuated and finally flushed with oxygen-free nitrogen. The mixture of salts remaining was dissolved in a small volume of cold air-free water (26 cc.) and enough standard acid was added to make an approximately 1% solution in 1 *N* acid (75 cc. of 1.3 N hydrochloric acid). This solution was then forced over by means of a pressure of nitrogen into a polariscope tube for determination of the optical rotation. The values found are given in Table II.

TABLE II

ROTATION OF CYSTEINE PREPARATIONS

Cystine $\alpha^{D}_{26°}$	*Wt. of cystine reduced, g.*	α^{D}, *calcd. as cysteine*	Evidence of decomposition[a]
205°	0.2699	12^{23}	Negative
205°	4.2352	5^{23}	Slightly positive
208°	2.0580	4^{28}	Slightly positive
208°	0.8065	5^{28}	Negative
208°	1.2341	$3''$	Negative
208°	1.3456	7^{30}	Slightly positive
208°	1.1203	5^{31}	Slightly positive

[a] Tested by bubbling pure nitrogen through the solution and passing the gases obtained through a solution of neutral cadmium sulfate.

When the salt remaining after evaporation of the ammonia was acidified directly, it was found that considerable decomposition with the liberation of hydrogen sulfide and the formation of a cloudy solution took place. This decomposition could be reduced and in many cases entirely prevented by the use of an ice-salt cooling bath during the addition of the acid to the water solution. The liberation of hydrogen sulfide during the reduction of cystine with zinc and hydrochloric acid has been mentioned by Okuda.[12] In a few experiments in which cystine was reduced with tin and hydrochloric acid, we have also found small amounts of hydrogen sulfide to be liberated.

Preparation of Cysteine Hydrochloride and Free Cysteine.—The preparation of pure cysteine hydrochloride involves its separation from the sodium chloride and small amounts of ammonium chloride present in the reaction mixture. The reduction as described above is carried out in a Dewar test-tube and the ammonia solution evaporated to dryness. The sodium salt remaining is dissolved in a small amount of cold 95% alcohol and then acidified with cold 2 *N* alcoholic hydrochloric acid. The precipitate of sodium chloride is filtered and washed several times with alcoholic hydrochloric acid. The filtrate and washings are evaporated to dryness at 45° under diminished pressure in an atmosphere of nitrogen, and the residue recrystallized from a small volume of hot 20% hydrochloric acid; 3.44 g. of pure cysteine hydrochloride was obtained from 10 g. of cystine. An approximately 1% solution of this product in 1 *N* hydrochloric acid had an optical rotation of 4.4" at 28°.

Preparation of Cysteine.—Free cysteine may be prepared by dissolving the hydrochloride in a small volume of absolute alcohol at room temperature and neutralizing with a solution of ammonia in absolute alcohol. The precipitate of free cysteine is filtered, washed with alcohol and ether and remains as a white powder. On standing an aqueous solution of this material deposits a white precipitate, which when recrystallized from dilute acid with sodium hydroxide gives characteristic hexagonal plates of cystine.

Summary

Cystine is soluble in liquid ammonia and can be reduced readily by metallic sodium in this medium. The reduction product has been shown to be cysteine.

A new method for the preparation of cysteine has been worked out on the basis of this reaction.

Benzylcysteine was prepared by adding benzyl chloride directly to the liquid ammonia solution of cysteine which had been prepared by the sodium reduction method. This procedure offers an exceptionally convenient method for preparing this and similar derivatives.

URBANA, ILLINOIS

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[12] Okuda, J. Biochem., 5, 220 (1925).

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE.
IX. ALKALI FUSION OF SOME DERIVATIVES OF ROTENONE

BY H. L. HALLER AND F. B. LAFORGE

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The rotenone molecule is generally assumed to consist of two component parts joined by a chain of carbon atoms containing the carbonyl group. On treatment with alcoholic potassium hydroxide, tubaic acid, a monohydroxy monocarboxylic acid of formula $C_{12}H_{12}O_4$ is obtained, which is converted into isotubaic acid[1] (rotenic acid) by fusion with potassium hydroxide or by treatment with sulfuric acid, Isotubaic acid is obtained directly by alkali fusion of rotenone or from isorotenone either by fusion or by treatment with alcoholic potassium hydroxide. Butenandt[1] has assumed that the rotenone molecule is cleaved at the carbonyl group either by hydrolysis or oxidation, because dihydrodesoxyrotenone, in which the carbonyl group is not present, is stable toward alkalies.

Tubaic and isotubaic acids are very closely related, differing from each other in the position of the reducible double bond. The characteristic nucleus of tubaic acid is assumed to be present in the rotenone molecule.

Of the four oxygen atoms of tubaic acid, two are contained in the carboxyl group, one is present as a hydroxyl group and the fourth cannot be brought into reaction and therefore is assumed to be in the form of an ether linkage, in which form it is also supposed to be present in rotenone itself.

In a previous article[2] we reported that isotubaic acid is formed from derritol under the same conditions as from rotenone. This fact seems remarkable since all six of the oxygen atoms in derritol can be characterized with certainty, as it had been shown that derritol contains no indifferent oxygen but a phenolic group in addition to the original carbonyl, lactone and two methoxyl groups of rotenone.[3] The acid which Butenandt obtained in minute quantity by boiling derritol in strong alcoholic potassium hydroxide solution may have been tubaic acid.[1] In the process of fusion the tubaic acid which is first formed is isomerized into isotubaic acid.

Since all the oxygen atoms in derritol are accounted for, it must follow that the indifferent oxygen in isotubaic acid is formed in the process of

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[1] In this article we have used the word isotubaic acid instead of rotenic acid for the reason that the hydroxyl derivative obtained by elimination of the carboxyl group was named rotenol by Takei after this word had been used by Butenandt, *Ann.*, 464, 253 (1928), *to* designate the zinc alkali reduction product of rotenone. This older name should be retained and the more logical isotubaic acid and isotubanol substituted for the terms rotenic acid and rotenol.

[2] H. L. Haller and F. B. LaForge, THIS JOURNAL, 52, 2480 (1930).

[3] (a) A. Butenandt, *Ann.*, 464, 253 (1928); (b) F. B. LaForge and L. E. Smith, THIS JOURNAL, 52, 1088 (1930).

fusion and that the characteristic grouping of tubaic acid is not part of the derritol molecule, but must be regarded as a secondary decomposition product. Whether or not the nucleus of tubaic acid is actually part of the rotenone molecule is therefore open to doubt, even though the isomerization of rotenone to isorotenone and of tubaic to isotubaic acid may be due to the shifting of a double bond in the side chain, as is now generally accepted.

These considerations led us to subject a number of characteristic rotenone derivatives to the alkali fusion process in order to determine which of them yielded acids of the tubaic acid type.

The method employed was in all cases essentially the same as that described for the preparation of isotubaic acid from rotenone.[2,4]

Both derritol and isoderritol[6] yielded isotubaic acid but the yield was less in the case of isoderritol. Dehydrorotenone[1] also gave isotubaic acid. Dihydroxyrotenonic acid, $C_{23}H_{24}O_8$ (Derris saure, Butenandt) and its isomer, isodihydroxyrotenonic acid, which on oxidation with hydrogen peroxide in alkaline solution yield derric acid,[6] also gave isotubaic acid on alkali fusion.

Rotenol (Butenandt),[1] which is supposed to contain no carbonyl group but a secondary alcoholic group in its place, contrary to our expectation, gave a yield of isotubaic acid three times greater than that obtained from rotenone.

It has been generally assumed that the carboxyl group in tubaic and isotubaic acids arises from the ketone group in rotenone which joins the two halves of the molecule, one of which corresponds to tubaic acid and the other to derric acid. The fact that isotubaic acid is easily obtained from rotenol on fusion with alkali contradicts this assumption. The possibility that the hydroxyl group is oxidized to the ketone group during the fusion process still remains, but the smooth manner in which the fusion proceeds, the slight amount of charring which takes place, and the greater yield of isotubaic acid incline us to doubt that this has happened.

On fusion of dihydroderritol methyl ether,[3b] a small quantity of a methoxyl-free phenolic acid was obtained which melted at 186° and gave the same color reaction with ferric chloride as did isotubaic acid. However, when this acid was mixed with isotubaic acid the melting point was twenty degrees lower than the melting point of isotubaic acid, and it could be sharply distinguished from isotubaic acid by an optical examination of the crystals, as well as by its different solubility in 40% alcohol. In another attempt to obtain a larger quantity of this acid, five grams of dihydroderritol methyl ether was fused with alkali under slightly different conditions, but in this case dihydrotubaic acid was obtained.

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[4] S. Takei, *Biochem. Z.*, 157, 1 (1925).

[5] F B. LaForge and L. E. Smith, THIS JOURNAL, 51,2574 (1929).

[6] F. B. LaForge and L. E. Smith, *ibid.*, 52, 1091 (1930).

All the derivatives mentioned above contain either the original lactone group of rotenone, or, as in the case of the two dihydroxyrotenonic acids, the hydrolyzed lactone group.

The lactone group of rotenone and most of its derivatives may also be opened by catalytic hydrogenation, with the formation of acids.[5] By this process rotenonic acid, $C_{23}H_{24}O_6$, is obtained from rotenone and corresponding acids are obtained by this reaction from dehydrorotenone, rotenol and derritol methyl ether.[3b] Except in the case of rotenone, the double bond originally present is also reduced by this process, and the dihydro acids are obtained. Several acids of this type were fused with potassium hydroxide in the usual manner, but in no case could isotubaic or dihydrotubaic acid be obtained. In most of the experiments only a very small quantity of a crystalline product could be isolated from the reaction mass, and in the case of rotenonic acid, the acid obtained could not be crystallized.

In the case of dehydrodihydrorotenonic acid[6] and dihydrorotenolic acid[3b] a small quantity of a phenolic acid was obtained, but it was definitely established by crystallographic methods that it was neither isotubaic acid nor dihydrotubaic acid.

Such of the above-mentioned compounds as gave isotubaic or dihydrotubaic acids contain the lactone group, or this group has been opened by hydrolysis, and it may be concluded that the hydroxyl group resulting from the opening of the lactone ring is necessary for the formation of isotubaic or dihydrotubaic acid.

The fact that isotubaic acid is obtained from rotenol (Butenandt) contradicts the theory that cleavage takes place at the carbonyl group, and the results as a whole indicate that tubaic acid may be a secondary cleavage product of rotenone.

Experimental

Alkali Fusion of Derritol.—Two grams of derritol was intimately mixed with 2 g. of finely powdered potassium hydroxide in a nickel crucible, and 1 cc. of water was added. Eighteen grams of powdered potassium hydroxide was then added, and the mixture heated in a metal-bath. The reaction mass was held at 205–210° for one hour with constant stirring. The temperature of the metal-bath was 250–270°. The melt was then slowly poured onto cracked ice and the resulting dark reddish-brown solution was saturated with carbon dioxide. The solution, after being filtered to remove a small quantity of tarry matter which sometimes separated, was acidified with dilute sulfuric acid and extracted four times with ether. The combined ether extracts were dried over sodium sulfate and the ether was removed. The remaining tarry residue was extracted with boiling petroleum ether (b. p. 57–70°). On concentrating this extract, isotubaic acid was obtained. The yield was 0.2 g. It was recrystallized from 40% alcohol. It melted at 184° and its optical properties[7] were identical with those of isotubaic acid. A mixture of this substance and isotubaic acid obtained from isorotenone had a melting point of 183°.

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[7] We are indebted to Mr. George L. Keenan of the Food and Drug Administration for the determination of the optical properties.

The conditions described for the alkali fusion of derritol were duplicated as closely as possible in the fusion of the other compounds.

Alkali Fusion of **Rotenol.**—Two grams of rotenol on fusion at *200–210"* for one-half hour yielded *0.65* g. of substance. After recrystallizing from *40%* alcohol, it melted at 184°, and its optical properties were identical with isotubaic acid. When it was mixed with authentic isotubaic acid, the melting point was *184°*.

Alkali Fusion of **Isoderritol.**—Two grams of isoderritol was fused in the manner described for derritol except that the water was omitted. The fusion temperature was 205°, which was maintained for one-half hour. The yield of substance from petroleum ether was about *0.1* g. After recrystallizing from *40%* alcohol, it melted at 182°, and its optical properties could not be differentiated from those of isotubaic acid. When it was mixed with isotubaic acid, the melting point was 182°.

Alkali Fusion of Dihydroderritol Methyl Ether.—Two grams of dihydroderritol methyl ether was fused in the usual manner at 205° for one-half hour. The acid obtained from petroleum ether was recrystallized from *25%* alcohol. It melted at about *174"* and lost carbon dioxide at 180°. The melting point varied with the rate of heating. It was methoryl free. In alcohol solution it gave a blue color with ferric chloride which could not be differentiated from the color given by isotubaic acid under the same conditions. However, its optical properties did not agree with those of isotubaic acid, and when it was mixed with isotubaic acid the melting point was *160°*.

Anal. Subs., *0.0214:* required *1.08* cc. $N/10$ alkali; *0.0204* g. subs. required *1.01* $N/10$ alkali; acid number calcd., *198, 201.*

In an attempt to prepare a larger quantity of this acid, *5* g. of dihydroderritol methyl ether was fused, but dihydrotubaic acid was obtained. The acid melted at *168"* and a mixture of this acid and dihydrotubaic acid had a melting point of *168"*.

Alkali Fusion of Dihydroxyrotenonic Acid.—Two grams of acid was fused at 205° for one-half hour in the usual manner except that the water was omitted. The acid obtained melted at 184° and was identified as isotubaic acid by its optical properties and its melting point when mixed with isotubaic acid.

Alkali Fusion of Isodihydroxyrotenonic Acid.—This substance when fused in the usual manner yielded isotubaic acid, which was identified in the manner described above.

Alkali Fusion of **Dehydrorotenone.**—Two and one-half grams of dehydrorotenone on fusion in the usual manner at 205° for one-half hour yielded isotubaic acid, which was identified as described above.

Alkali Fusion of Rotenonic Acid.—Two grams of rotenonic acid was fused in the manner described above with and without the addition of water, but in no instance was it possible to obtain a crystalline derivative. Dihydrorotenonic acid behaved similarly.

Alkali Fusion of Dehydrodihydrorotenonic Acid.—Two grams of dehydrodihydrorotenonic acid on fusion in the usual manner yielded a small quantity of acid, which was recrystallized from dilute alcohol. It melted somewhat indefinitely at 175°. Its crystallographic properties were totally different from those of dihydrotubaic acid.

Alkali Fusion of Dihydrorotenolic Acid.—Two grams of dihydrorotenolic acid was fused in the usual manner at 205° for half an hour. On recrystallization from dilute alcohol a very small quantity of acid was obtained which melted at 159° but not sharply. When mixed with dihydrotubaic acid the melting point was 135–140°, with previous softening at 125°. The optical properties of the compound were found to be different from those of dihydrotubaic acid.

Summary

Several derivatives of rotenone have been submitted to the alkali fusion process.

Derritol, isoderritol, rotenol, dihydroxyrotenonic acid and isodihydroxyrotenonic acid on alkali fusion yielded isotubaic acid.

Rotenonic acid, as well as several other derivatives of rotenone in which the lactone group was opened by catalytic reduction, did not give isotubaic or dihydrotubaic acid on fusion with alkali.

Compounds which gave isotubaic or dihydrotubaic acid contain the lactone group or this group has been opened by hydrolysis. The conclusion is drawn that the hydroxyl group resulting from the opening of the lactone ring is necessary for the formation of isotubaic or dihydrotubaic acid.

The fact that rotenol gives isotubaic acid contradicts the theory that cleavage of the molecule takes place at the ketone group.

The nucleus of tubaic acid does not exist in derritol as such, but is a secondary decomposition product. Perhaps it does not exist in rotenone.

Substance	Product of alkali fusion
Derritol	Isotubaic acid
Isoderritol	Isotubaic acid
Rotenol	Isotubaic acid
Dihydroxyrotenonic acid	Isotubaic acid
Isodihydroxyrotenonic acid	Isotubaic acid
Dehydrorotenone	Isotubaic acid
Dihydroderritol methyl ether	Dihydrotubaic acid
Rotenonic acid	....
Dehydrodihydrorotenonic acid	Unidentified phenolic acid
Dihydrorotenolic acid	Unidentified phenolic acid

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

THE COMPOSITION OF SALKOWSKI'S ARABAN

BY C. L. BUTLER AND LEONARD H. CRETCHER

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Introduction

Most of the methods devised in the attempt to prepare pure xylans have involved the use of alkaline copper solutions in the process of purification.[1]

It was shown by Salkowski that no precipitate was formed when Fehling's reagent was added to a solution of gum arabic, but that on further addition of sodium hydroxide a precipitation was brought about. The substance precipitated was hydrolyzed with 2% sulfuric acid and formed large amounts of arabinose. On oxidation of the hydrolysate with nitric acid, there was no evidence of the formation of mucic acid. Because of these facts, Salkowski called the substance an araban.

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[1] Salkowski, Z. *physiol. Chem.,* 34, 162 (1901); 35, 240 (1902); 117, 48 (1921); Henser and Braden, J. *prakt. Chem.,* 103, 69 (1921); 104, 259 (1922); Link, THIS JOURNAL. 51,2506 (1929); 52, 2091 (1930).

Inasmuch as the original gum is known to contain galactose, the precipitation with copper would naturally seem to be a method for the concentration of the arabinose present in the gum. In fact, the procedure has been used with this end in view.[2]

Though xylans have been prepared which were largely if not wholly polymers of xylose, most of the arabans are known to form other sugars as well as arabinose on hydrolysis.[3] It is probable that the pentosan obtained from beet pectin by Ehrlich[4] is more nearly a true araban than any described previously. This substance gave 90.8% of crystalline arabinose on hydrolysis.

In order to throw further light on a rather confused subject, we have reinvestigated Salkowski's araban. It was analyzed according to methods given by Van der Haar.[5] The results obtained show that the so-called araban contains even less arabinose than arabic acid (the ash-free gum). For purposes of comparison, the analysis of the araban and of arabic acid are given in Table I.

TABLE I

ANALYSES

	Araban	Arabic acid
Pentose (as arabinose)	28.8	34.4
Methyl pentose (as rhamnose hydrate)	12.7	14.2
Hexose (galactose)	41.1	42.1
Uronic acid (glucuronic)[a]	19.5	15.5
Total	102.1	106.2

[a] That the methylpentose and aldehyde acid in gum arabic are rhamnose and glucuronic acid, respectively, was shown by the present authors [Butler and Cretcher, THIS JOURNAL, 51,1519 (1929)].

The presence of glucuronic acid has been confirmed by Weinmann[6] and by Heidelberger and Kendall.[7]

Experimental Part

Preparation of **Salkowski's** Araban.—One hundred grams of gum arabic was dissolved in 2 liters of warm distilled water. To the warm solution was added one liter of Fehling's solution (made by mixing 500 cc. of solution containing 34.65 g. of copper sulfate crystals and 500 cc. of solution containing 125 g. of potassium hydroxide and 175 g. of Rochelle salt). The alkaline copper solution of gum arabic was stirred while concentrated sodium hydroxide solution (300 g. per liter) was added until no further precipitation took place. About 500 cc. of alkaline solution was required. The precipitate

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[2] For example, see Onslow, "Practical Plant Biochemistry," second edition, p. 55.

[3] Kurt Hess, "Die Chemie der Zellulose," Leipzig, 1928, p. 46.

[4] Ehrlich and Sommerfeld. *Biochem. Z.*, 168,299 (1926).

[5] Van der Haar, "Anleitung zum Nachweis zur Trennung und Bestimmung der Monosaccharide und Aldehydesauren," Berlin, 1920, pp. 61, 71, 123.

[6] Weinmann, *Ber.*, 62, 1637 (1929).

[7] Heidelberger and Kendall, *J. Biol. Chem.*, *84,639* (1929).

settled in a few minutes. The blue mother liquor was decanted and the blue precipitate was pressed between cotton cloth and filter paper. It was dissolved in 150 cc. of 1:1 hydrochloric acid and precipitated by the addition of one liter of 95% alcohol. The precipitate was allowed to settle and the alcoholic liquor was then decanted. The precipitate was washed with three successive portions of alcohol. It was redissolved in 100 cc. of water and again precipitated by alcohol. The product was washed and dried for several hours in vacuum at 70°. The samples weighed 51 g. and contained only traces of copper. $\alpha = -2.85°$ where $l = 2$ and $C = 3.94$; $(\alpha)_D$ −36.2°.

Anal. Subs., 0.982: CO_2 (Lefèvre method), 0.0435. Found: 4.43% CO_2, equivalent to 19.5% uronic acid. Subs., 0.491: mucic acid, 0.134. Found: galactose, 41.1. Subs., 0.491: alcohol-soluble furfural phloroglucid, 0.033; alcohol insoluble furfural phloroglucid, 0.155. From the latter figure was deducted 0.032 g. to allow for the phloroglucid due to uronic acid.[8] Found: methyl pentose (as rhamnose hydrate), 12.7; pentose (as arabinose), 28.8.

Summary

The araban of Salkowski has been shown not to be a simple polymer of arabinose but to contain arabinose, galactose, rhamnose and glucuronic acid in about the same proportion as they are present in ash-free gum arabic.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON PYRIMIDINES. CXVIII. MOLECULAR REARRANGEMENTS IN THE THYMINE SERIES

BY W. SCHMIDT-NICKELS[1] AND T. B. JOHNSON

RECEIVED AUGUST 8, 1930 PUBLISHED NOVEMBER 5, 1930

Hilbert and Johnson discovered that 2,6-dimethoxypyrimidine interacts with bromo-acetoglucose giving an acetyl derivative which is converted by hydrolysis into a 3-glucoside of uracil,[2] namely, "*glucuridine*." This fact was the incentive to develop the present paper, which deals with new rearrangements in the thymine series.

Thymine	I	$\mathrm{NHCONHCH{=}C(CH_3)CO}$
2,6-Dichloro-5-methylpyrimidine	II	$\mathrm{NCCl{=}NCH{=}C(CH_3)CCl}$
2,6-Dimethoxy-5-methylpyrimidine	III	$\mathrm{NC(OCH_3){=}NCH{=}C(CH_3)C(OCH_3)}$
2-Oxy-3,5-dimethyl-6-methoxypyrimidine	IV	$\mathrm{NCON(CH_3)CH{=}C(CH_3)C(OCH_3)}$
2,6-Dioxy-3,5-dimethylpyrimidine	V	$\mathrm{NHCON(CH_3)CH{=}C(CH_3)CO}$

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[8] Ref. 5, p. 75.

[1] Chemical Foundation Research Fellow, 1929-1930.

[2] Hilbert and Johnson, Science, 69, 579 (1929); THIS JOURNAL, 52, 200 (1930).

2,6-Dioxy-1,3,5-trimethylpyrimidine	VI	$\overline{\mathrm{N(CH_3)CON(CH_3)CH{=}C(CH_3)C}}\mathrm{O}$
2,6-Diethoxy-5-methylpyrimidine	VII	$\overline{\mathrm{NC(OC_2H_5){=}NCH{=}C(CH_3)C}}\mathrm{(OC_2H_5)}$
2-Oxy-3,5-dimethyl-6-ethoxypyrimidine	VIII	$\overline{\mathrm{NCON(CH_3)CH{=}C(CH_3)C}}\mathrm{(OC_2H_5)}$
2-Oxy-3-ethyl-5-methyl-6-ethoxy-pyrimidine	IX	$\overline{\mathrm{NCON(C_2H_5)CH{=}C(CH_3)C}}\mathrm{(OC_2H_5)}$
2,6-Dioxy-3-ethyl-5-methylpyrimidine	X	$\overline{\mathrm{NHCON(C_2H_5)CH{=}C(CH_3)C}}\mathrm{O}$

The work was started with the investigation of 2,6-dimethoxy-5-methylpyrimidine, III, which is described by Gerngross,[3] who made it by reduction of 2,6-dimethoxy-4-chloro-5-methylpyrimidine with zinc dust and hydrochloric acid. The same compound was, however, prepared for our work by another method. Starting with thymine I, 2,6-dichloro-5-methylpyrimidine II was made by treatment with phosphorus oxychloride as described by Steudel and Kossel[4] and the latter then converted into 2,6-dimethoxy-5-methylpyrimidine III by the action of sodium methylate. We now find that the imido ester linkages in this compound are very susceptible to change, and the methyl groups show a great tendency to migrate to the adjacent nitrogen atoms of the pyrimidine ring. By heating at 200° for forty-eight hours a quantitative rearrangement to 1,3-dimethyl-thymine VI is obtained. Interaction with methyl iodide led to the formation of 2-oxy-3,5-dimethyl-6-methoxypyrimidine IV. The structure of this compound follows from the fact that it gives 3-methylthymine V quantitatively when the methoxy group is destroyed by hydrolysis with hydrochloric acid.

After having discovered this characteristic behavior of 2 6-dimethoxy-5-methylpyrimidine III, we hoped to obtain a nucleoside of thymine by treatment of this pyrimidine with bromo-acetoglucose according to the technique of Hilbert and Johnson. The result was, however, the formation of 3-methylthymine V. It was assumed that by addition of bromo-acetoglucose to the pyrimidine nitrogen in the 3-position a small amount of the nucleoside was probably formed, the bromine and the adjacent methyl attached to oxygen in the 2-position then combining to form methyl bromide. This methyl bromide adds to the 3-nitrogen, whereupon more methyl bromide is formed and the process is continued until the rearrangement is complete and a 3-methylated compound is formed instead of the desired glucoside of thymine.

Guided by the above conception of reaction mechanism, it was thought that by replacing the methyl bromide by the less active methyl chloride, the addition of the alkyl halide might be depressed, affording a better chance for the addition of the sugar. So chloro-acetoglucose was used instead of bromo-acetoglucose; but here, also, no reaction product of the

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[3] Gerngross, Ber., **38,** 3408 (1905).

[4] Steudel and Kossel, *Z. physiol. Chem.*, 29, 303 (1900).

desired constitution was obtained, When the temperature of reaction was raised from 50 to 100° the mixture underwent decomposition.

Keeping in mind the synthesis of a thymine nucleoside, the methyl group was next replaced by the ethyl group and this led to the synthesis and investigation of 2,6-diethoxy-5-methylpyrimidine VII. This compound, prepared from 2,6-dichloro-5-methylpyrimidine II and sodium ethylate, had a lower melting point (36') than 2,6-dimethoxy-5-methylpyrimidine III, which fact made the compound useful for attempts to melt it together with bromo-acetogfucose or chloro-acetoglucose.

Our first observation was that 2,6-diethoxy-5-methylpyrimidine VII differed considerably from 2,6-dimethoxy-5-methylpyrimidine III in so far as its behavior at high temperatures was concerned. While the methyl compound was completely rearranged at 200° in forty-eight hours, the corresponding ethyl compound was stable under the same conditions. It was, however, observed that methyl iodide acted in the same way as in the case of 2,6-dimethoxy-5-methylpyrimidine III: 2-oxy-3,5-dimethyl-6-ethoxypyrimidine VIII was formed. Its structure follows from the fact that 3-methyl-thymine V was formed by digesting the pyrimidine with hydrochloric acid. The action of ethyl iodide was also studied and the expected substance, 2-oxy-3-ethyl-5-methyl-6-ethoxypyrimidine IX was obtained. This was converted by hydrolysis with hydrochloric acid into 3-ethyl-thymine X.

Since ethyl bromide would be the probable by-product of a reaction between 2,6-diethoxy-5-methylpyrimidine VII and bromo-acetoglucose, and since it was found by experimentation that ethyl bromide does not react with 2,6-diethoxy-5-methylpyrimidine, it was concluded that the reaction between this pyrimidine and bromo-acetoglucose might be of promise for the formation of the desired nucleoside of thymine. By heating the compound with the sugar derivative at 50° for seven days, we obtained a very small amount of a crystalline substance which melted at 316° after recrystallization from alcohol. The amount was, however, too small for investigation. Chloro-acetoglucose did not react with 2,6-diethoxy-5-methylpyrimidine VII, as might 'have been expected from the experiment with the corresponding methyl compound.

All the pyrimidines prepared in the course of this work are easily obtained in a high state of purity. Three of the compounds described (III, V, VI) were already known but prepared by other methods. In each of these cases our compounds showed a higher melting point. With the exception of 1,3-dimethyl-thymine VI, which can be prepared more easily and just as pure by methylation of thymine with methyl sulfate, we believe that we have shown the easiest way for the preparation of absolutely pure alkyl derivatives of thymine. The study of pyrimidine rearrangements will be continued in this Laboratory.

Experimental Part

Preparation of Thymine, I.—Thymine, from which all the compounds described in this paper were prepared, was synthesized by the method of Wheeler and Merriam[5] by condensing ethyl pseudothiourea with the sodium salt of ethyl formylpropionate in aqueous solution, and hydrolysis of the resulting 2-ethylmercapto-5-methyl-6-oxypyrimidine with hydrochloric acid. It was observed, however, that the yield of thymine was best when the mixture of ethyl formate and ethyl propionate was added to the suspension of sodium in dry ether immediately and not added slowly as stated in the original directions for carrying out the ester condensation. Thirty-seven grams of thymine was obtained in one operation by using 46 g. of sodium in 1 liter of ether, 229.5 cc. of ethyl propionate, 240.5 cc. ethyl formate and 92 g. of ethyl pseudothiourea hydrobromide. The same proportions of reagents gave only 27 g. of thymine when the original directions were followed.

2,6-Dichloro-5-methylpyrimidine, II.—The method employed for the preparation of this compound was essentially that of Steudel and Kossel[6] with slight variations in technique. Twenty grams of thymine was heated with 80 cc. of phosphorus oxychloride at 110-120° for five hours, whereafter the excess of phosphorus halide was removed by heating at 80° under vacuum. The cooled residue was then dissolved in ether, the ethereal solution washed with water and dilute sodium carbonate solution and finally dried over sodium sulfate. The pyrimidine was finally purified by distillation and boiled at 108-109° at 11 mm. It melted at 25-26° and the yield was 21.5 g.

2,6-Dimethoxy-5-methylpyrimidine, III.—Twenty grams of the dichloropyrimidine II was dissolved in 100 cc. of methyl alcohol and the liquid poured into a solution of 7 g. of sodium in 100 cc. of methyl alcohol, whereupon sodium chloride separated immediately, the mixture becoming warm. The reaction was complete after heating for five minutes and after filtering from sodium chloride and distilling off excess of alcohol, the resulting oil was dissolved in ether, washed with sodium hydroxide solution and then dried over anhydrous sodium sulfate. On evaporating the solvent the pyrimidine separated in crystalline form. It was purified further by crystallization from petroleum ether and melted at 61°. The yield was 15.5 g.

Anal. Calcd. for $C_7H_{10}O_2N_2$: C, 54.51; H, 6.54; N, 18.17. Found: C, 54.33; H, 6.50; N, 18.14, 18.04.

Rearrangement of the Pyrimidine III into its Isomer 1,3-Dimethylthymine, VI.—Five grams of the pyrimidine III were heated in a sealed tube at 200° for forty-eight hours, when the rearrangement into the alkylated thymine was complete. The pyrimidine was purified by recrystallization from alcohol and melted at 155°.[7] The absence of methoxy groups was proved by recovering the unchanged pyrimidine melting at 155° after evaporation with strong hydrochloric acid.

Anal. Calcd. for $C_7H_{10}O_2N_2$: C, 54.51; H, 6.54; N, 18.17. Found: C, 54.60; H, 6.54; N, 18.06, 18.27.

2-Oxy-3,5-dimethyl-6-methoxypyrimidine, IV.—This compound is easily obtained by allowing 2,6-dimethoxy-5-methylpyrimidine to interact with methyl iodide at ordinary temperature. Solution of the pyrimidine takes place immediately and within fifteen minutes crystals of the rearranged pyrimidine begin to separate. The reaction was complete after fifteen hours. This pyrimidine crystallized from a mixture of alcohol and ether in the form of needles melting at 144°.

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[5] Wheeler and Merriam, *Am. Chem. J.*, 29, 478 (1903); see also Harkins and Johnson, THIS JOURNAL, 51, 1237 (1929).

[6] Steudel and Kossel, *Z. physiol. Chem.*, 29, 393 (1900).

[7] Johnson and Clapp, *J. Biol. Chem.*, 5, 60 (1908).

Anal. Calcd. for $C_7H_{10}O_2N_2$: C, 54.51; H, 6.54; N, 18.17. Found: C, 54.53; H, 6.63; N, 18.04, 18.09.

When this compound was warmed in aqueous hydrochloric acid solution it was converted quantitatively into 3-methyl-thymine V. The latter crystallized from hot water in the form of needles melting at 291°. Johnson and Clapp[8] reported a melting point of 280–282°.

Anal. Calcd. for $C_6H_8O_2N_2$: C, 51.40; H, 5.76; N, 20.00. Found: C, 51.39; H, 5.69; N, 20.00, 19.96.

2,6-Diethoxy-5-methylpyrimidine, VII.—From 21.5 g. of 2,6-dichloro-5-methylpyrimidine II and sodium ethylate (7.5 g. Na) by interaction in alcohol solution. The pyrimidine crystallizes from alcohol and melts at 36° to an oil. The yield was 16.5 g.

Anal Calcd. for $C_9H_{14}O_2N_2$: C, 59.30; H, 7.75; N, 15.38. Found: C, 59.39; H, 7.80; N, 15.24, 15.55.

An attempt was made to rearrange this pyrimidine into its corresponding nitrogen substituted derivative by heating at 200° for forty-eight hours. Slight decomposition resulted from this treatment, but the greater part of the pyrimidine was recovered, melting at 35". There was no evidence of any molecular rearrangement having taken place.

2-Oxy-3,5-dimethyl-6-ethoxypyrimidine, VIII.—A solution of 3. g. of the pyrimidine VII in 2.1 cc. of methyl iodide was allowed to stand at room temperature for four days. The crystalline substance which separated in excellent yield was purified by crystallization from a mixture of alcohol and ether and melted at 111° to an oil. The structure of this compound was established by the fact that it was converted into 3-methyl-thymine by hydrolysis with boiling hydrochloric acid solution.

Anal. Calcd. for $C_8H_{12}O_2N_2$: C, 57.10; H, 7.20; N, 16.67. Found: C, 57.02; H, 7.18; N. 16.62.

2-Oxy-3-ethyl-5-methyl-6-ethoxypyrimidine, IX.—This compound is formed by molecular rearrangement when 2,6-diethoxy-5-methyl-pyrimidine VII is dissolved in ethyl iodide and the solution allowed to stand for seven days. The pyrimidine was obtained in the form of colorless needles when crystallized from ether, and melted at 78°. Attempts to bring about this same rearrangement of the pyrimidine VII by the use of ethyl bromide were unsuccessful. No change was observed after remaining in contact with an excess of ethyl bromide for two weeks.

Anal. Calcd. for $C_9H_{14}O_2N_2$: C, 59.30; H, 7.75; N, 15.38. Found: C, 59.46; H, 7.81; N, 15.54.

2,6-Dioxy-3-ethyl-5-methylpyrimidine or 3-Ethyl-thymine, X.—This pyrimidine was formed when the compound IX was dissolved in hydrochloric acid and the solution evaporated to dryness. It crystallized from hot water in needles which melted at 223°.

Anal. Calcd. for $C_7H_{10}O_2N_2$: C, 54.51; H, 6.54; N, 18.17. Found: C, 54.42; H, 6.53; N, 18.36.

Attempts to Prepare Glucosidic Derivatives of the Pyrimidine Thymine

1.—A mixture of 2 g. of 2,6-dimethoxy-5-methylpyrimidine and 2 g. of bromoacetoglucose was heated at 60° for forty-eight hours. The resulting product was then extracted three times with 5 cc. of water and then with ether at room temperature. A small quantity of crystalline material did not dissolve and was identified as 3-methylthymine. A large quantity of this same pyrimidine also deposited as the aqueous extract was allowed to stand. In other words, a rearrangement of methyl from oxygen

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[8] Johnson and Clapp, J. *Biol.* Chem., 5, 57 (1908).

to nitrogen in the pyrimidine ring had been effected by the action of the halogenated glucose compounds.

2.—A second experiment was carried out with chloro-acetoglucose by heating this with the pyrimidine at 50° for eight days and then for one week at 100°. The mixture darkened considerably during this treatment and only a very small amount of an undefined product was left after the extraction with ether.

3.—Experiments 1 and 2 were repeated with 2,6-diethoxy-5-methylpyrimidine using both bromo- and chloro-acetoglucose, respectively. The mixtures were heated at 50° for seven days and in the case of the bromo-acetoglucose experiment a small amount of material was finally separated which crystallized from alcohol and melted at 316° but the quantity obtained was too small for further investigation. The second experiment with chloro-acetoglucose did not lead to the formation of any product which could be identified.

Summary

1. 2,6-Dimethoxy-5-methylpyrimidine and 2,6-diethoxy-5-methylpyrimidine were synthesized.

2. 2,6-Dimethoxy-5-methylpyrimidine rearranged quantitatively to 1,3-dimethyl-thymine at 200° in forty-eight hours. 2,6-Diethoxy-5-methyl pyrimidine was stable under these conditions.

3. 2,6-Dimethoxy-5-methylpyrimidine gave with methyl iodide 2-oxy-3,5-dimethyl-6-methoxypyrimidine. 2,6-Diethoxy-5-methylpyrimidine gave with methyl iodide 2-oxy-3,5-dimethyl-6-ethoxypyrimidine and with ethyl iodide 2-oxy-3-ethyl-5-methyl-6-ethoxypyrimidine. Ethyl bromide did not react.

4. 3-Methyl-thymine was obtained from 2-oxy-3,5-dimethyl-6-methoxypyrimidine and from 2-oxy-3,5-dimethyl-6-ethoxypyrimidine by treatment with hydrochloric acid. 3-Ethyl-thymine was obtained from 2-oxy-3-ethyl-5-methyl-6-ethoxypyrimidine and hydrochloric acid.

5. 2,6-Dimethoxy-5-methylpyrimidine and bromo-acetoglucose gave 3-methyl-thymine. Chloro-acetoglucose did not react. 2,6-Diethoxy-5-methylpyrimidine and bromo-acetoglucose gave a substance, m. p. 316°, the quantity of which was too small for investigation. Chloro-acetoglucose did not react.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

RESEARCHES ON CHLORIMINES. III. THE DECOMPOSITION OF CERTAIN AROMATIC ALD-CHLORIMINES TO FORM NITRILES. A METHOD FOR THE PREPARATION OF NITRILES FROM ALDEHYDES[1]

BY C. R. HAUSER AND A. G. GILLASPIE

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The first two papers of this series[2] have described the preparation of a number of aromatic ald-chlorimines. It was shown that these compounds decomposed spontaneously at varying rates into hydrogen chloride and a nitrile. In the present investigation a number of ald-chlorimines have been decomposed with bases to form nitriles.

Although the early workers[3] observed that benzalchlorimine readily decomposes into benzonitrile and hydrogen chloride, Raschig,[4] was the only one who recorded a yield of the nitrile. He reported that a 40% yield of benzonitrile (calculated from benzaldehyde) was obtained by subjecting the impure condensation product of benzaldehyde and monochloramine to steam distillation in the presence of sodium hydroxide.

Since the isolation of a number of ald-chlorimines has now been accomplished, a rather simple yet greatly improved method has been developed for the preparation of certain nitriles. The chlorimines in cold alcoholic solution are treated with an alcoholic solution of either potassium hydroxide or sodium ethylate. The sodium or potassium halide is rapidly precipitated even at 0°, and in some cases almost quantitative yields of the nitriles are produced. Table I (Experimental Part) shows the actual yields of nitriles obtained from seven chlorimines. The reaction may be represented by the equation $RCH{=}NCl + KOH \longrightarrow RCN + KCl + H_2O$. This represents a good method for the preparation of nitriles from aldehydes since the latter are readily converted into chlorimines in good yields.

In view of the fact that an acetyl derivative of an ald-oxime is considered to have a *syn* configuration[5] when it yields a nitrile on treatment with alkali, it would appear that the ald-chlorimines described in this paper have *syn* configurations, since the latter readily yield nitriles in an analogous manner. However, as only one of the two possible stereoisomeric ald-chlorimines has been isolated in each case, it would be premature to assign a *syn* configu-

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[1] This paper is constructed from portions of a thesis presented by A. G. Gillaspie in partial fulfilment of the requirements for the degree of Master of Arts in the Graduate School of Arts and Sciences, Duke University.

[2] Hauser and Hauser, THIS JOURNAL, 52, 2050 (1930); Hauser, Hauser and Gillaspie, *ibid.*, 52, 4158 (1930).

[3] Luxmoore, J. Chem. *Soc.*, 69, 191 (1896); Forster, ibid., 107, 265 (1915).

[4] Raschig, "Schwefel und Stickstoffstudien." 1924, p. 80.

[5] See Cohn, "Organic Chemistry for Advanced Students," Part II, 1928, p. 306.

ration to these compounds, for the other isomers if isolated might also be able to react with alkalies to form nitriles. Furthermore in cases where acetyl *anti* ald-oximes are hydrolyzed by alkalies to form oximes, the CH_3COO- group is replaced by hydroxyl, whereas chlorine attached to nitrogen in chloramines and other compounds[6] apparently is not hydrolyzed in this manner. Thus the decomposition of ald-chlorimines by alkalies to form nitriles does not necessarily indicate a *syn* configuration.

Although the decomposition of the chlorimine by the base was rapid in every case, it was plainly evident, by observing the rate of precipitation of the halide salt, that anisal- and piperonalchlorimines were decomposed at a lower rate than the other five compounds described in this paper. By analyses for active chlorine it was shown that o-chlorobenzalchlorimine was completely decomposed by sodium ethylate at 0° within one and one-half minutes, whereas anisalchlorimine was only 43% decomposed under similar conditions within two minutes, and not completely decomposed until after five minutes. This is rather significant since o-chlorobenzalchlorimine in the pure state is much more stable than anisalchlorimine. These observations suggest the study of the decomposition of ald-chlorimines by weaker bases such as amines, as here the reaction rate would doubtless be slow enough to measure more precisely. This work is now in progress.

Experimental

The ald-chlorimines used for the preparation of nitriles were prepared from aldehydes and monochloramine[7] according to the methods described in the first two papers of this series.[2] They were purified by recrystallization from alcohol and dried on a porous plate.

Preparation of Nitriles.—A sample (1.50 to 2.00 g.) of chlorimine is dissolved in the smallest possible amount of alcohol at room temperature and then cooled in an ice-bath. In cases where the chlorimine is sparingly soluble in alcohol a small quantity of acetone[8] will facilitate solution. To the cooled solution of the chlorimine is added a cold concentrated alcoholic solution of 1.25 equivalents of sodium ethylate or potassium hydroxide, and the mixture allowed to stand for several minutes or until the halide salt no longer precipitates. Sufficient cold water is then added to dissolve the halide salt and precipitate as much of the nitrile as possible. After filtering, more of the nitrile may be obtained by extracting the filtrate with small portions of ether, and evaporating the ether on a water-bath. The nitriles were dried in a vacuum desiccator, weighed and the yields calculated. The results are given in Table I. Several of the low yields could doubtless be increased if carried out on a large scale. After recrystallization from petroleum ether, the nitriles were identified by their melting points and by hydrolysis to the corresponding acids.

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[6] Sidgwick, "The Electronic Theory of Valency," 1927, p. 158.

[7] The method of preparation of monochloramine is described by Coleman and Hauser, THIS JOURNAL, 50, 1195 (1928). This is a modification of the method of Marckwald and Wille, *Ber.*, 56, 1319 (1923).

[8] Acetone solutions of the nitrochlorimines became deeply colored when treated with the base, and the crude nitriles obtained in these cases possessed a darker color than when only alcohol was used as solvent.

TABLE I

PERCENTAGE YIELDS OF NITRILES

Chlorimine	Base used			
	Sodium ethylate		Potassium hydroxide	
	(1)[a]	(2)[b]	(3)[a]	(4)[b]
Anisal-	81	94	77	95
o-Chlorobenzal-	73	85	70	83
Piperonal-	79	96	85	97
2-Chloro-5-nitrobenzal-	51	82		
p-Chlorobenzal-	47	60		
m-Nitrobenzal-	54	82		
o-Nitrobenzal-	60	70		

[a] Yields of nitrile obtained by precipitating with water only. [b] Total yields of nitrile obtained.

The yields of nitriles given in Table I were obtained from chlorimines which had been purified by recrystallization from alcohol. Excellent yields of good products have been obtained from several crude chlorimines when the latter were decomposed with sodium ethylate. Good yields of nitriles are obtained when calculated from the aldehydes, since yields of 80–85% of chlorimines calculated from aldehyde used are readily obtainable in most cases.

Rates of Decomposition of *o*-Chlorobenzalchlorimine and Anisalchlorimine.—Approximately 0.1 molar alcoholic solutions of the chlorimines in separate flasks were treated with slightly more than the calculated amount of sodium ethylate in alcoholic solution (1 *M*) at 0°. Samples were pipetted off and analyzed for active chlorine. o-Chlorobenzalchlorimine was completely decomposed within one and a half minutes, while anisalchlorimine was only 43% decomposed after two minutes and completely decomposed after five minutes.

Summary

A number of aromatic ald-chlorimines have been decomposed by sodium ethylate or potassium hydroxide in alcoholic solution to form good yields of nitriles. This represents a method for the preparation of nitriles from aldehydes, since the latter are readily converted into ald-chlorimines.

DURHAM, NORTH CAROLINA

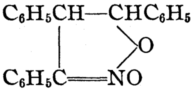
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

ISOXAZOLINE OXIDES. X. REDUCTION

BY E. P. KOHLER AND A. R. DAVIS

RECEIVED AUGUST 12, 1930 PUBLISHED NOVEMBER 5, 1930

In order to complete the work on isoxazoline oxides it was desirable to make a more careful study of their behavior toward reducing agents. Two of these oxides have been reduced, heretofore, both of them with zinc and acetic acid. Kohler and Barrett[1] added two atoms of hydrogen to triphenyl isoxazoline oxide (A) and interpreted the product as an hydroxy isoxazolidine (B); but it was found later[2] that the substance is, in reality, an hydroxy oxime (C).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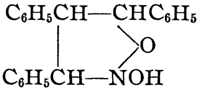
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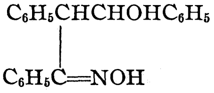
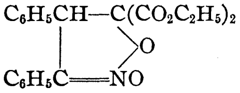


$$\begin{array}{l} C_6H_5CHCHOHC_6H_5 \\ \qquad | \\ C_6H_5C{=}NOH \end{array}$$

C

Kohler and Barrett[3] also reduced the ethyl ester of an isoxazoline oxide dicarboxylic acid (D). Here again the reaction stopped with the addition of two atoms of hydrogen, and the product was likewise regarded as an hydroxy isoxazolidine (E). The evidence on which this formula was based is, however, no longer conclusive, and it now seems at least as probable that the substance is the hydroxy oxime (F).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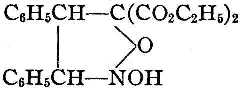
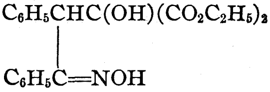

E



$$\begin{array}{l} C_6H_5CHC(OH)(CO_2C_2H_5)_2 \\ \qquad | \\ C_6H_5C{=}NOH \end{array}$$

F

We selected for reduction the ketonic isoxazoline oxide III, and decided to reduce it in steps, in order to note the result of a competition for hydrogen by the three reducible components, the carbonyl group, the unsaturated system C=NO, and the oxide group. Since bases very rapidly transform these ketonic oxides into other reducible substances, reduction in alkaline media was not attempted. These oxides are fairly stable in the presence of dilute acids but all attempts at reducing our substance with metal and acid ended in insoluble polymerization products too complex to unravel; reduction in acid media therefore did not prove feasible.

In view of the circumstances which have been described it became necessary to resort to catalytic hydrogenation in neutral solution. Preliminary experiments both with Willstatter's platinum black and with Adams' platinum oxide showed that while the hydrogenation occurs in stages which proceed at different rates, the stages overlap and that there is

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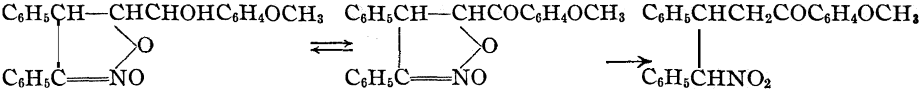
[1] Kohler and Barrett, THIS JOURNAL, 46, 2105 (1924)

[2] Kohler and Richtmyer, ibid., 52, 2038 (1930).

[3] Kohler and Barrett, *ibid.*, 48, 1770 (1926).

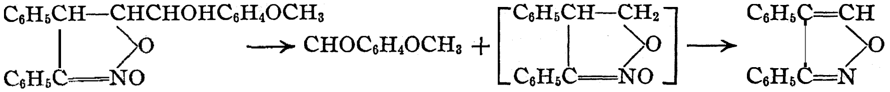
no sharp break in the curve representing the speed of hydrogen absorption. Later operations were therefore carried out in an apparatus with which it was possible to measure the absorbed hydrogen with great accuracy and the process was interrupted as soon as one mole of hydrogen had been consumed. Under these circumstances the product was composed almost entirely of the three substances VIII, IX and X.



VIII and IX III X

The relative amounts of the stereoisomeric carbinols VIII and IX varied slightly with the conditions, but, to our surprise, these two substances constituted by far the largest part of the primary reduction products. Thus in a typical experiment we obtained 55% of the higher-melting isomer VIII, 20% of the lower-melting isomer IX, 5% of X, and 20% of an oil which doubtless was composed largely of secondary products.

No less surprising is the generation of a nitro group by hydrogenation, but the proof of the structure of these primary reduction products is explicit. The nitro compound X is identical with the product obtained by adding phenyl nitro methane to benzal acetyl anisole. The other two reduction products, VIII and IX, liberate iodine from potassium iodide and chlorine from phosphorus pentachloride; they are, therefore, still oxides. Moreover, chromic acid removes the two hydrogen atoms that have been added and oxidizes the reduction products to the oxide from which they came, while potassium hydroxide cleaves them to anisic aldehyde and 3,4-diphenyl isoxazole.

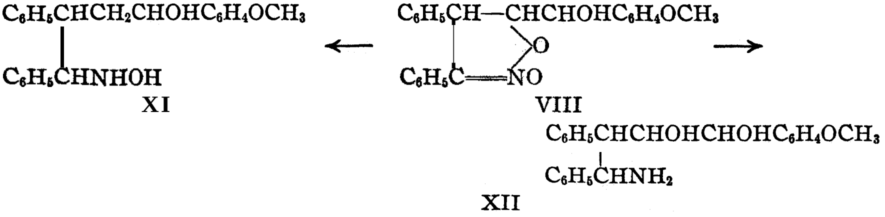


VIII XIII

These new oxides, on further hydrogenation, absorb hydrogen more slowly but with great regularity until six additional atoms have been consumed. The solution then deposits a sparingly soluble compound which is formed in accordance with the equation

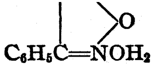
$$C_{23}H_{21}O_4N + 6H = C_{23}H_{25}O_3N + H_2O$$

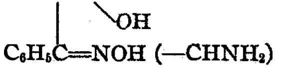
It is not possible to isolate any intermediate between the oxide and this final reduction product. If the operation is stopped short of this final stage, a corresponding quantity of oxide is recovered. For this final reduction product only two formulas have any probability. The formation of a substance with this composition manifestly involves the opening of the isoxazole ring. If this occurred between the oxygen and the carbon atom in the 5-position, as it does in the formation of X, the product would be the hydroxylamine derivative XI. But it is at least equally probable that the ring is opened in the same manner as it is in triphenyl isoxazole, and this would lead to the formula of the amine XII. Since the reduction product is not only a strong base but also is not oxidized by Fehling's solution it evidently is not the hydroxylamine derivative



These results show quite conclusively that the hydrogen combines far more rapidly with the carbonyl group than it does with any part of the system C=NO. Combined with what had been learned heretofore by the reduction of isoxazoline oxides with metal and acid, they show also that the first step in the reduction is not removal of oxygen, as is the case with amine oxides,[4] azoxy compounds[6] and open-chained nitrones.[6] Nor is it 1,3-addition of hydrogen to the unsaturated system in the manner of the reaction between isoxazoline oxides and Grignard reagents.?

It seems not unlikely that the first step in the reduction of all types of oxido compounds is the same. These substances in reality contain an unsaturated oxygen atom. The primary stage in the reduction may well be the addition of hydrogen to this unsaturated oxygen atom; what happens subsequently depends upon the rest of the molecule. In the amine oxides and related substances, loss of water is inevitable because every possible rearrangement product would be unstable; in the isoxazoline oxides the primary product can undergo rearrangement to a stable oxime which may subsequently be reduced to an amine.





Experimental Part

Preparation and Proof of Structure

The starting point in the preparation of the oxide was an addition product previously obtained from benzal acetyl anisole and phenyl nitromethane.[8]

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[4] Bamberger, Ber., 32, 342 (1899); Dunstan and Goulding, *J. Chem. Soc.*, *75*, 792 (1899).

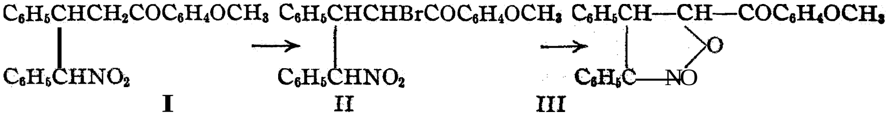
[5] Werigo, Ann., 165, 202 (1873).

[6] Angeli, *Atti Accad. Lincei*, 20, I, *546* (1911).

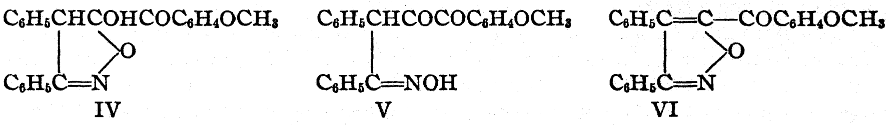
[7] Kohler and Richtmyer. THIS JOURNAL. 52, 2038 (1930).

[8] Kohler and Allen, *ibid.*, 50, 884 (1928).

This substance, on bromination, gave a mixture of α-bromo compounds from which hydrogen bromide was eliminated with pyridine,



In proof that the compound thus obtained is an isoxazoline oxide, it was established that potassium acetate isomerizes it to an hydroxy isoxazoline (IV), and that bases convert it both into an open-chained triketone oxime (V) and also into an isoxazole derivative (VI). These are characteristic reactions of isoxazoline oxides.



Bromination: **α-Anisoyl-α-bromo-β,γ-diphenyl-γ-nitro** Propane (II).—A solution of 100 g. of pure dry addition product in hot chloroform was brominated with 45 g. of bromine. At first only a few drops of bromine were added, the solution was boiled until the color disappeared, then the remainder was dropped into it as fast as it decolorized without further heating. When the solution is boiled during the bromination, and excess of bromine is allowed to accumulate in it, more than one equivalent of bromine is consumed and the product contains a polybromide which interferes with subsequent operations. After recrystallization from chloroform–methyl alcohol, the bromo compound melts at 165°. The crude product melting at 163° is sufficiently pure for nearly all purposes.

Anal. Calcd. for $C_{23}H_{20}O_4NBr$: C, 60.8; H, 4.4. Found: C, 60.5; H, 4.6.

3,4-Diphenyl-5-anisoyl Isoxazoline Oxide (III).—A suspension of 100 g. of the finely ground α-bromo compound in 500 cc. of 95% alcohol and 70 g. of pyridine was heated to boiling. Solution was complete in fifteen minutes but the boiling was continued for another ten minutes. On cooling, the isoxazoline oxide separated from the pale purple solution. The crystalline material was collected on a filter, washed with 95% alcohol, then with dilute hydrochloric acid until free from pyridine, and finally with water until free from chloride. The first filtrate and the alcohol washings, on concentration and acidification, yielded 11 g. of crude product which gave 8 g. of recrystallized oxide, making the total yield 79 g. or 92%.

Absolute alcohol gave the same yield as 95% alcohol, but absolute methyl alcohol was found to be unsatisfactory because the reaction was very much slower at the lower boiling point. By recrystallization from chloroform–methyl alcohol the oxide was obtained in colorless needles melting at 158°. It is readily soluble in chloroform, sparingly soluble in methyl alcohol. It can be recrystallized without change from glacial acetic acid, does not reduce permanganate in acetone and is not affected by boiling with sodium dichromate in glacial acetic acid. It liberated iodine from potassium iodide in glacial acetic acid, and it liberated a mixture of chlorine and nitrosyl chloride when heated with phosphorus pentachloride.

Anal. Calcd. for $C_{23}H_{19}O_4N$: C, 74.0; H, 5.1. Found: C, 73.7; H, 5.2.

Rearrangement: 3,4-Diphenyl-5-hydroxy-5-anisoyl **Isoxazoline** (IV).—A solution containing 2 g. of the oxide, 1 g. of potassium acetate and a few drops of glacial acetic acid in 20 cc. of dry methyl alcohol was boiled for an hour. It deposited the crystalline rearrangement product when cooled. The hydroxyl compound is, however, most conveniently prepared directly from the α-bromo compound. For this purpose 15 g. of finely powdered bromo compound was suspended in a mixture of 325 cc. of methyl alcohol, 500 cc. of water, 20 g. of sodium hydroxide, and 200 cc. of ether. The mixture was shaken until all the bromo compound was in solution—about thirty minutes—then acidified with acetic acid and allowed to stand at room temperature for half an hour. It deposited 10 g. of the hydroxyl compound. This was pale yellow in color but on recrystallization from chloroform–methyl alcohol, it became colorless and melted at 177°.

Anal. Calcd. for $C_{23}H_{19}O_4N$: C, 74.0; H, 5.1. Found: C, 74.1; H, 5.1.

The hydroxyl compound was readily soluble in chloroform, sparingly soluble in methyl alcohol. It crystallized from alcohol in colorless prisms, and from ether–petroleum ether in hexagonal plates. It crystallized unchanged from glacial acetic acid. Sodium peroxide oxidized it to anisic acid and diphenyl isoxazolone.

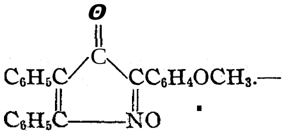
The Benzoate.—Like the hydroxy isoxazolines described in earlier papers in this series, our substance resisted all attempts to methylate it, but it was readily turned into a benzoate. To a solution of 1 g. of the substance in 5 cc. of dry pyridine. 1 cc. of benzoyl chloride was added. The pink solution was kept at room temperature for two hours, during which a solid separated. The mixture was diluted with water, acidified with hydrochloric acid and extracted with ether. The washed and dried solution, on evaporation, deposited the benzoate in silky needles which melted at 173°.

Anal. Calcd. for $C_{30}H_{23}O_5N$: C. 75.5; H, 4.8. Found: C, 75.3; H, 4.6.

α-Anisyl-γ,ϑ-diphenyl-butane-trione Oxime (V).—The yellow oxime is formed by the action of alkalies on both the oxide and the hydroxy isoxazoline, but it is most readily prepared directly from the α-bromo compound. To this end the bromo compound is treated exactly as in the preparation of the hydroxy isoxazoline, but the yellow solution is acidified rapidly with iced hydrochloric acid instead of acetic acid. The yield is 74%.

Anal. Calcd. for $C_{23}H_{19}O_4N(C_2H_5)_2O$: C, 72.5; H, 6.5. Found: C, 72.3; H, 6.6.

Like all other substances of this type that are known, the oxime crystallizes in yellow prisms containing one molecule of ether. It melts with decomposition at 110°. When a methyl alcoholic solution of the oxime is boiled with a little potassium acetate and acetic acid, it is transformed almost quantitatively into the hydroxy isoxazoline, and when a drop of hydrochloric acid is added to a solution of the oxime in chloroform, it turns purple and soon deposits a purple nitrone.



2-Anisal-3-keto-4,5-diphenyl Pyrrolenine Oxide, .—The purple nitrone crystallizes from the chloroform solution in fluffy needles melting at 182° with decomposition.

Anal. Calcd. for $C_{23}H_{17}O_3N$: C, 77.8; H, 4.8. Found: C, 77.7; H, 5.1.

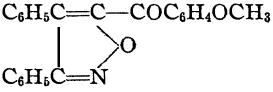
3,4-Diphenyl-5-anisoyl Isoxazole **(VI).**—The isoxazole is formed by the action of bases on the α-bromo compound, the polybromides, the isoxazoline oxide, the hydroxy isoxazoline and the triketone oxime; it represents the final degradation product of all of these substances by weak bases or dilute alkalies. In quantity, it is most conveniently obtained by suspending the α-bromo compound in methyl alcohol, adding an equal weight of potassium acetate and boiling the mixture. The bromo compound soon dissolves and isoxazole begins to separate in compact crystals along with potassium bromide. Since these solids cause serious bumping, it is necessary to filter from time to time and repeat the boiling, but in the end the yield of isoxazole is 94%.

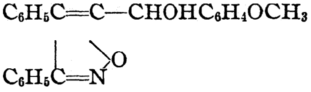
Anal. Calcd. for $C_{23}H_{17}O_3N$: C, 77.7; H, 4.7. Found: C, 77.3; H, 4.9.

The isoxazole crystallizes in needles which melt at 156°. When pure it is quite colorless, but it usually has a pale yellow color which cannot be removed by recrystallization.

II. Reduction

We examined the behavior toward reducing agents of the isoxazoline oxide, the hydroxy isoxazoline and the isoxazole. With zinc and acid all these substances except the isoxazole gave very sparingly soluble substances which were evidently condensation as well as reduction products. The isoxazole, however, readily combined with two atoms of hydrogen, being reduced to a substance which liberated a mole of gas from methyl magnesium iodide and which chromic acid reoxidized to the isoxazole—therefore evidently the carbinol ring is intact.


VI


VII

Hydrogenation in the presence of platinum likewise gave only complex products with the hydroxy isoxazoline and the yellow oxime, but with the isoxazoline oxide it gave mainly monomolecular products.

Reduction of the Isoxazole.—To a solution of 10 g. of the isoxazole in glacial acetic acid, which was heated on a steam-bath, zinc dust was added in small quantities over a period of two hours. The mixture was filtered, and the filtrate diluted with water, then extracted with ether. The extract, freed from acetic acid, dried and evaporated, deposited a small quantity of solid amid considerable oil which was presumably an acetate. The oil was boiled with methyl alcoholic potassium hydroxide for a short time, the solution diluted with water and extracted with ether. The ether now deposited the solid carbinol; yield, 6.8 g. By recrystallization from carbon tetrachloride–petroleum ether, the substance was obtained in colorless prisms which melted at 146".

Anal. Calcd. for $C_{23}H_{19}O_3N$: C, 77.3; H, 5.3. Found: C, 76.6; H, 5.5.

Oxidation.—To 0 5 g. of the carbinol in 10 cc. of glacial acetic acid, sodium bichromate was added gradually until there was no further evidence of reduction. The mixture was diluted with water and extracted with chloroform. The extract was washed, dried and concentrated, then diluted with methyl alcohol. It deposited 0.35 g. of pure isoxazole.

Reduction of the Oxide.—For the purpose of reduction the oxide was repeatedly recrystallized from the same "reagent methyl alcohol" that was used as solvent in the reductions. The reductions were carried out under atmospheric pressure with a specially constructed apparatus with which it was possible to determine the absorbed hydrogen with great accuracy. The catalyst was Adams' platinum oxide.

In a typical experiment a suspension of 2 g. of the finely ground oxide and 0.2 g. of the catalyst in 100 cc. of methyl alcohol was shaken with hydrogen, using the calibrated apparatus. The oxide was completely in solution after ten minutes. By that time the solution had absorbed 124.9 cc. of hydrogen instead of 120 cc. calculated for two atoms and the operation was stopped immediately.

The yellow solution was decanted from most of the catalyst, filtered and boiled down to about a fourth of its volume. In order to remove a small quantity of colloidal platinum which made trouble unless it was removed at this point, a small quantity of active charcoal was added a few minutes before the boiling was discontinued. The solution was then filtered again and set aside. It deposited a solid which proved to be composed almost entirely of the high-melting reduction product VIII. It was purified by recrystallization from methyl alcohol; yield, 1.1 g.

The filtrate was allowed to evaporate to dryness. It deposited a mixture of large transparent prisms and long silky needles which were separated by hand and purified separately. The prisms (0.4 g.) were found to be a stereoisomer (IX) of the high-melting reduction product and the needles (0.1 g.) were identified as the nitro compound (I).

3,4-Diphenyl-5-(a-hydroxy-4-methoxy-benzyl) Isoxazoline Oxide, VIII.—The higher-melting reduction product crystallized from methyl alcohol in flat needles that melted without decomposition at 170°.

Anal. Calcd. for $C_{23}H_{21}O_4N$: C, 73.6; H, 5.6. Found: C, 73.6; H, 6.0.

The substance liberated iodine from potassium iodide and chlorine from phosphorus pentachloride as readily as did the original oxide.

Oxidation.—To a solution of 0.5 g. of the reduction product in boiling glacial acetic acid, sodium bichromate was added in small quantities until the red color of the bichromate appeared in the solution. The mixture was poured into water, which precipitated a solid product. After recrystallization from methyl alcohol, the solid melted at 156°, and the melting point was not changed when mixed with the original oxide; yield, 0.4 g.

Cleavage.—A suspension of 3 g. of the reduction product and 1 g. of solid potassium hydroxide in 20 cc. of methyl alcohol was boiled for thirty minutes. The yellow solution was diluted with water and extracted with ether. The washed and dried ethereal layer, when evaporated, left an oil. This was divided into two portions. To the first were added phenylhydrazine and a few drops of acetic acid. It deposited a solid which after purification melted at 122° and which was identified as the phenylhydrazone of anisic aldehyde by comparison with a sample made from the aldehyde.

The second half of the oil was dissolved in ether and freed from the aldehyde by means of saturated sodium bisulfite. The ethereal solution was washed with bicarbonate, dried and evaporated. It left an oil, but a solution of this oil in petroleum ether deposited a solid. which melted at 91° and was identified as diphenyl isoxazole. This will be described later.

The Stereoisomeric Reduction Product, IX.—The lower-melting reduction product behaved exactly like the substance which has just been described, liberating iodine from potassium iodide with the same ease and giving the same oxidation and cleavage products It crystallized from methyl alcohol in six-sided prisms and melted at 160°.

Anal. Calcd. for $C_{23}H_{21}O_4N$: C, 73.6; H, 5.6. Found: C, 73.7; H, 5.7.

Reduction of the New Oxide VIII: α,β-Diphenyl-γ,ϑ-dihydroxy-ϑ-anisyl Butyl Amine, XII.—Quantitative experiments showed that the new oxides are reduced much more slowly than the ketonic compound and that there is no break in the curve representing the rate at which hydrogen is absorbed until six atoms have disappeared. Moreover, an examination of the result of interrupting the process before six atoms of hydrogen had been used showed that all intermediates between the oxide and the final product are more rapidly reduced than the oxide.

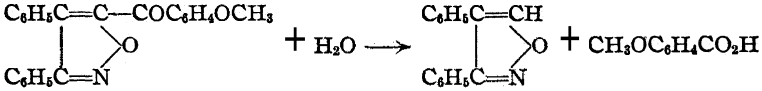
Thus 2 g. of the oxide VXII in 100 cc. of methyl alcohol was shaken with hydrogen in the presence of 0.2 g. of platinum until 120 cc. had been absorbed. This required about two hours. The solution, manipulated in the usual manner, yielded 1.2 g. of the starting material and 0.5 g. of reduction product. Allowing for loss during crystallization, this quantity of reduction product corresponds to the absorption of six atoms of hydrogen.

In another experiment, 2 g, of the same oxide was reduced completely in seven hours and six atoms of hydrogen were used in the process. The product, isolated in the usual manner, crystallized in needles melting at 208°.

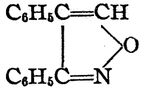
Anal. Calcd. for $C_{23}H_{25}O_3N$: C, 76.0; H, 6.9; mol. wt., 363. Found: C, 76.1; H. 6.8; mol. wt., 349.

III. Diphenyl Isoxazole

Inasmuch as the reduction product of anisoyl diphenyl isoxazoline oxide is easily cleaved by alkalies, it seemed worth while to study the behavior of the isoxazole itself because a similar cleavage of this substance would result in a type of disubstituted isoxazole, for which no methods of preparation are known.



It was found that while this cleavage does not take place very readily it can be accomplished and that the yield may be brought to 88%. The structure of the isoxazole was established by ozonization, which led to a product that was hydrolyzed to β-benzil monoxime. Like all other isoxazoles which are not completely substituted, **3,4-diphenyl** isoxazole can be further cleaved with alkalies. The mode of cleavage is similar to that of those mono-substituted isoxazoles which have no substituent in the 5-position.

3,4-Diphenyl Isoxazole,  ⟶ $C_6H_5CH_2CO_2H + C_6H_5C{\equiv}N$.—A suspension of 10 g. of diphenyl anisoyl isoxazole in 50 cc. of 5% ethyl alcoholic potassium hydroxide was boiled for half an hour, then filtered. The operation was repeated with the unchanged isoxazole which had been collected on the filter until none of it was left. The alcoholic filtrates on dilution deposited the new isoxazole as a flocculent precipitate. It was dried and recrystallized from low-boiling petroleum ether; yield 5.5 g. or 88%.

Anal. Calcd. for $C_{15}H_{11}ON$: C 81.4; H, 5.0. Found: C, 81.9; H, 5.1.

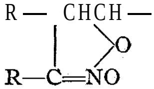
The isoxazole is readily soluble in all organic solvents. It crystallizes from low-boiling petroleum ether in colorless needles which melt at 91.

Ozonization.—A current of ozonized oxygen containing about 6% of ozone was passed through a solution of 0.5 g. of the isoxazole in ethyl bromide for one and one-half hours. Addition of water and removal of solvent left a cream-colored oil, which was dissolved in 10% aqueous sodium hydroxide. The alkaline solution was extracted with ether, then gradually neutralized with carbon dioxide. It deposited a crystalline solid which was identified as the β-monoxime of benzil by comparison with a sample on hand.

Alkaline Cleavage.—A solution of 2 g. of the isoxazole in 20 cc. of 5% methyl alcoholic potassium hydroxide was boiled for two hours, then diluted with water and extracted with ether. The ethereal solution was dried over sodium sulfate and cautiously evaporated. It left an oil which had the odor of benzonitrile and which when boiled with 10% aqueous sodium hydroxide gave benzoic acid. The alkaline solution, from which the benzonitrile had been removed, was acidified and again extracted with ether. The dried extract left an oil when evaporated, but a solution of this oil in petroleum ether deposited a solid melting at 75°. This was identified as phenylacetic acid by comparison with a sample.

Summary

1. When a ketonic isoxazoline oxide



is hydrogenated it first takes up two atoms of hydrogen at the carbonyl group and forms a new oxide.

2. The reduction of isoxazoline oxides in which there is no carbonyl group doubtless always gives an open-chained hydroxy oxime as the first product; but in catalytic hydrogenations these oximes are reduced to amines.

3. 3,4-Disubstituted isoxazoles, heretofore unknown, can be prepared by cleaving ketonic isoxazoles with bases. When these 3,4-disubstituted isoxazoles undergo further cleavage, they behave like those mono-substituted isoxazoles which have no substituent in the 5-position.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

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

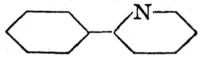
STEREOCHEMISTRY OF PHENYLPYRIDINE COMPOUNDS: THE PREPARATION AND INVESTIGATION OF 2-(2-CARBOXY-6-CHLOROPHENYL)-PYRIDINE-3-CARBOXYLIC ACID AND 3-(2-CARBOXYPHENYL)-6-PHENYLPYRIDINE-2,4-DICARBOXYLIC ACID. X.[1]

BY CATHERINE CASSELS STEELE[2] AND ROGER ADAMS

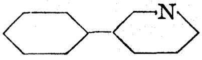
RECEIVED AUGUST 14, 1930 PUBLISHED NOVEMBER 5, 1930

A natural corollary to the development of the study of the optical isomerism exhibited by certain types of substituted diphenyl compounds is an investigation of binuclear compounds similar to diphenyl, and of these the dipyridines and the phenylpyridines resemble diphenyl most closely.

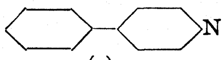
In the case of the phenylpyridines, only one ring—the pyridine nucleus—is different, and they may be divided into three classes; (a) where the N is "ortho," (b) where it is "meta" and (c) where it is "para" to the carbon atom linked to the phenyl nucleus.



(a)



(b)



(c)

Type (a) differs from (b) and (c) in the fact that there cannot be four

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[1] For the last two papers in this series, see (a) Stanley and Adams, THIS JOURNAL, 52, 4471 (1930); (b) Browning and Adams, *ibid.*, 52, 4098 (1930).

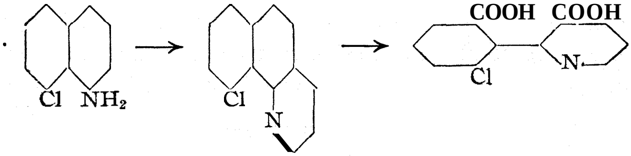
[2] Commonwealth Fund Fellow.

substituent groups in the "ortho" position, and any trisubstituted phenylpyridine of the type (a) will not be directly comparable with the corresponding trisubstituted diphenyl, as the fourth position is not occupied by a hydrogen atom. If the obstacle theory[1a,3] is correct and on the assumption that a pyridine ring resembles in structure a benzene ring, this difference would be unlikely to affect resolution except in so far as a blocking group of size 0.94 to 1.04 Å.[4] is eliminated. If, however, Bell and Kenyon's[5] modified view that the electrical character of the substituting groups has an added influence besides the effective size of the electrical field of force of these groups, then the substituted phenylpyridines though conforming to all the requirements for resolution of the correspondingly substituted diphenyls, may exhibit a marked divergence in behavior.

Trisubstituted phenylpyridines of all three types and tetrasubstituted compounds of types (b) and (c) must be investigated, and various groups used to determine whether or not the calculated amount of interference[4] between such groups will give the same experimental results as the corresponding diphenyls. Neither has it been established that the five carbon atoms and the nitrogen are coplanar in pyridine. If the nitrogen is bent away from the plane of the five carbons, or if the whole ring is distorted, then in the (a) type the distances between the ortho positions in the two rings will be very different from those between identical groups in a diphenyl, and therefore the interference values will also differ.

The methods available for preparing ortho-substituted phenylpyridines of types (a) and (h) are very limited; in fact, the only satisfactory method yet found is the synthesis of substituted naphthoquinolines and then their oxidation to the corresponding phenylpyridine-dicarboxylic acids.

In this work, two acids were prepared: 2-(2-carboxy-6-chlorophenyl)-pyridine-3-carboxylic acid (III), which is of type (a), and 3-(2-carboxyphenyl)-6-phenylpyridine-2,4-dicarboxylic acid (V), of type (b). The first was obtained through a Skraup synthesis of 10-chloro-a-naphthoquinoline (II) from 8-chloro-1-naphthylamine (I), and subsequent oxidation with neutral permanganate, and the second by the oxidation of a-phenyl-β-naphthoquinoline-γ-carboxylic acid (diapurin) IV).



I II III

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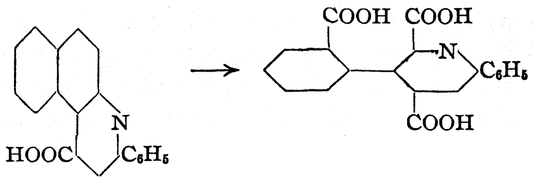
[3] Mills, *J. Soc. Chem.* Ind., 45, 884 (1926); Stanley and Adams, THIS JOURNAL, 52, 1200 (1930).

[4] Stanley and Adams, *ibid.*, 52, 1201 (1930).

[5] Bell and Kenyon, *J. Soc. Chem. Ind.*, 45,864 (1926).



IV V

It was found impossible to resolve either acid; of the chloro acid the following salts were investigated: di-strychnine, di-brucine, di-morphine, mono-cinchonine, di-cinchonine and mono-quinine, and of the tricarboxylic acid, the mono-strychnine, di-strychnine, mono-brucine, di-brucine and mono-cinchonine salts were prepared.

If x-ray data are taken into consideration using the values C–Cl, 1.89 Å.; C–COOH, 1.56 Å.; and C–C (2,2′ for the diphenyl system), 2.90 Å.;[4] in the case of the 2-(2-carboxy-6-chlorophenyl)-pyridine-3-carboxylic acid it is obvious that either the chlorine or carboxyl in the benzene ring should collide with the carboxyl in the pyridine ring and free rotation should be prevented (two carboxyls, 1.56 Å. + 1.56 Å. = 3.12 Å. − 2.90 Å. → + 0.22 Å.; one chlorine and one carboxyl, 1.56 Å. + 1.89 Å. = 3.45 Å. − 2.90 Å. → + 0.55 Å.). In the case of the 3-(2-carboxyphenyl)-6-phenylpyridine-2,4-dicarboxylic acid, similar conditions exist; the carboxyl in the phenyl ring should collide with either of the carboxyls in the pyridine nucleus.

These results may indicate distortion within the molecule with subsequent free rotation, due to the electrical attraction of the basic nitrogen and acid carboxyl groups. Two diastereoisomeric salts were in no case isolated. More types of phenylpyridines must be studied before speculation in regard to the stereochemical character of this class of compounds is extended. Other phenylpyridines and dipyridyls are under investigation in this Laboratory.

It should be noted that the di-brucine salt of the chloro acid gave zero rotation, while all the salts of the tricarboxylic (except the monocinchonine) gave zero rotations. These substances obviously fall into a group which show abnormalities similar to those compounds which Haworth believed demonstrated the existence of labile optical isomers.[6] Such a phenomenon is so general among alkaloidal salts' of many types that the authors believe such conclusions as were drawn by Haworth to be misleading.

Experimental Part

8-Chloro-1-naphthylamine.—The preparation was carried out in two steps. 8-Chloro-1-nitronaphthalene was prepared according to Ullmann and Consonno[8] by the

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[6] "Annual Reports." 24, 101 (1928).

[7] Hyde and Adams, THIS JOURNAL, 50, 2502 (1928).

[8] Ullmann and Consonno, Ber., 35, 2808 (1902); see also German Patent 99,758.

chlorination of 1-nitronaphthalene in 100-g. lots. The yield of the pure 8-chloro-1-nitro isomer after crystallization from benzene–ligroin was 23 g., m. p. 94–95°. The reduction of 8-chloro-1-nitronaphthalene by tin and hydrochloric acid described by Ullmann was very tedious and good results were not obtained. 8-Chloro-1-naphthylamine was, however, prepared in 97% yield by the following method.

An intimate mixture of 20 g. of 8-chloro-1-nitronaphthalene with 60 g. of iron powder and 30 cc. of water in a 500-cc. found-bottomed flask fitted with a reflux condenser was heated for ten minutes on the steam-bath and a few drops of concd. hydrochloric acid added through the condenser, the flask being well shaken. Heating was thereafter continued for seven hours with occasional shaking. With longer heating decomposition of the molecule becomes a factor, and with less time unreduced nitro compound is recovered. The mixture was cooled and the amine extracted with ethyl alcohol until the filtrate gave no precipitate with water. The alcoholic filtrate was poured into a large excess of water and the precipitate filtered. The latter was then dissolved in dilute hydrochloric acid, filtered from any nitro compound and the amine precipitated with ammonia. The amine separates from ligroin in small colorless needles which turn dark purple in color on exposure to the air; m. p. 95-96' (various values for the melting point are given in the literature; Ullmann, 89"; Atterberg, 93–94°).[9]

Anal. Calcd. for $C_{10}H_8NCl$: (Parr bomb) Cl, 20.00. Found: Cl, 19.93.

10-Chloro-α-naphthoquinoline.—The Skraup synthesis was carried out using arsenic acid as the oxidizing agent in the proportions given by Claus[10] for the conversion of α-naphthylamine to a-naphthoquinoline. To 59.5 g. of 8-chloro-1-naphthylamine in a 1-liter, 3-necked flask fitted with a mechanical stirrer, condenser and dropping funnel, were added 54.2 g. of arsenic acid (sp. gr. 2) and 178.7 g. of glycerol in the order named. Then 113.8 g. of concd. sulfuric acid was added gradually from the dropping funnel, the stirrer being started whenever the mixture became sufficiently liquid. The mixture was heated for one and one-half hours at 100° in an oil-bath, and then for nine hours at 170–180°. The material was poured while hot into a large excess of water and the precipitate allowed to settle overnight. The resinous precipitate was removed by filtration through an ordinary filter funnel and washed with water. The combined filtrates were placed in a 3-liter separatory funnel and a layer of ether followed by an ice-cold solution of 44 g. of potassium hydroxide (one-third the calcd. amount to neutralize the sulfuric acid used) in about 220 cc. of water was added. This ethereal extract consists almost entirely of resinous material. The aqueous layer was then treated similarly with a concd. solution of 88 g. of potassium hydroxide (the remaining two-thirds necessary for neutralization) and the precipitate extracted thoroughly with ether. The ether layer was dried over anhydrous magnesium sulfate and the ether removed. The yield of crude material was 47.5 g. A second run of 27.5 g. of chloronaphthylamine was made and the 17.5 g. of crude material obtained was added to the first product; the resulting 65 g. of crude material after two crystallizations from ligroin gave 26.8 g. with the constant, m. p. 81–82'. The insoluble material was re-extracted with boiling ligroin and 3.7 g. with a melting point of 81.5–82° was obtained. The total yield of pure **10-chloro-a-naphthoquinoline** was 30.5 g. (20%). It crystallized from ligroin in small, hard, bright yellow prisms, m. p. 81.5–82°.

Anal. Calcd. for $C_{13}H_8NCl$: Cl, 16.63. Found: Cl, 16.44.

2-(2-Carboxy-6-chlorophenyl)-pyridine-3-carbolic Acid.—Skraup and Cobenzl[11] found that oxidation of a-naphthoquinoline with chromic acid gave a-naphthoquinoline-

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[9] Ullmann, *Ber.*, 35, 2809 (1902); Atterberg, *ibid.*, 9, 1731 (1876).

[10] Claus, *J. prakt. Chem.*, [2] 57, 68 (1898).

[11] Skraup and Cobenzl, *Monatsh.*, 4,463 (1883).

quinone, while oxidation with permanganate at 40–50° gave a 70% yield of α-phenylpyridine-dicarboxylic acid. It was found possible to oxidize chloronaphthoquinoline to the dicarboxylic acid with permanganate but the higher temperature of 100" was necessary. The difficulty with such oxidations is the isolation of the acid, as there is no general method suitable for all the acids. After several attempts, the following method gave the best results. A mixture of 10 g. of chloronaphthoquinoline and 800 cc. of water was heated to 100° in a 3-liter, 3-necked flask fitted with a mechanical stirrer, condenser and dropping funnel. To the boiling mixture was added gradually from the dropping funnel a cold saturated solution of 21.8 g. of potassium permanganate (10% excess) in water. Decolorization of the permanganate was almost immediate and the addition was complete in forty-five minutes. The hot liquid was filtered from the manganese dioxide, the latter washed thoroughly with boiling water and the united filtrates allowed to cool. A small amount of unoxidized quinoline usually separated at this point and was removed by filtration. The solution was then made slightly acid with hydrochloric acid and evaporated to a very small volume on the steam-bath, when crystals of the dicarboxylic acid separated. The yield was 5 g. The acid was slightly colored and was purified by dissolving in alcohol, decolorizing with norit, and after concentration of the solution, diluting the latter with hot water until a slight cloudiness appeared. On cooling, the solution deposited small, colorless crystals of 2-(2-carboxy-6-chlorophenyl)-pyridine-3-carboxylic acid. They showed no sharp melting point, but turned dark around 240°, and completely melted at 252–256° with decomposition.

Anal. Calcd. for $C_{13}H_8O_4NCl$: Cl, 12.86. Found: Cl, 13.04.

The yields obtained in the synthesis of this acid may be summarieed as follows: 450 g. nitronaphthalene ⟶ 121.6 g.; 8-chloro-1-nitronaphthalene ⟶ 87 g.; 8-chloro-1-naphthylamine ⟶ 30.5 g.; 10-chloro-a-naphthoquinoline ⟶ 15 g.; **chlorophenylpyridine-dicarboxylic** acid.

Alkaloid Salts of Chlorophenyl-pyridine-dicarboxylic Acid

Di-strychnine Salt.—Warm methyl alcohol solutions of 1.2 g. of acid and 2.87 g. of strychnine were mixed and evaporated to dryness. The hard amorphous solid so obtained crystallized slowly from hot water in large, translucent parallelogram plates. These on exposure to the air effloresced to give a white powder which was dried in a desiccator, m. p. 171–173'. The first fraction, consisting of 1 g. (one-fourth of the total salt) had the specific rotation $[\alpha]_D$ −21.37° in chloroform, and on a second crystallization had $[\alpha]_D$ —25.45". A second fraction from the original mother liquors gave $[\alpha]_D$ −25.3°, and the final mother liquor on evaporation to dryness gave a salt with $[\alpha]_D$ —21.16'.

Rotation. 0.3041 g. made up to 25 cc. with chloroform at 20° gave α_D = —0.52'; $l = 2$; $[\alpha]_D$ —21.37".

Anal. Calcd. for $C_{55}H_{52}O_8N_5Cl$: neut. equiv., 472.7. Found: 473.6.

One gram of the salt was decomposed with dilute ammonia and the strychnine removed by extraction with chloroform. The aqueous solution of the ammonium salt of the acid was evaporated to dryness and showed no optical activity in aqueous solution.

Di-brucine Salt.—The di-brucine salt was made in and crystallized from methyl alcohol. Clusters of long, slender, colorless needles separated and effloresced in air. They were powdered and dried in air; m. p. 168–170°. All the fractions isolated as well as the mother liquors had zero rotation. The salt also crystallized from ethyl acetate in small hard prisms, but no change in rotation was observed.

Anal. Calcd. for $C_{59}H_{60}O_{12}N_5Cl$: Cl, 3.33. Found: Cl, 3.53.

Di-morphine Salt.—This salt was made in methyl alcohol and did not crystallize readily from any of the ordinary solvents. Crystals were obtained by dissolving the salt in the minimum amount of hot ethyl alcohol and adding hot ethyl acetate until one more drop turned the solution cloudy. On cooling, small, colorless crystals separated, m. p. 200–204°. Six fractions in all were isolated, and had the same rotation in absolute methyl alcohol.

Rotation. 0.1067 g. made up to 25 cc. with methyl alcohol at 20° gave an = –0.589"; $l = 2$; $[\alpha]_D$ –69.06°.

Anal. Calcd. for $C_{47}H_{46}O_{10}N_3Cl$; Cl, 4.19. Found: Cl, 4.26.

Mono-cinchonine Salt;-—This was prepared in methyl alcohol, and crystallized from a large volume of ethyl acetate in small colorless prisms, m. p. 154–156°. Three fractions were isolated and the salt in the mother liquors recovered. All gave the same rotation.

Rotation. 0.1014 g. made up to 20 cc. with absolute methyl alcohol at 20° gave $\alpha_D = +0.763°$; $l = 2$; $[\alpha]_D$ +75.2°.

The first fraction, consisting of a gram of salt, was decomposed by shaking with dilute ammonia and chloroform in a separatory funnel. The ammonium salt solution was evaporated to dryness. It gave zero rotation.

Di-cinchonine Salt.—Methyl alcohol solutions of the acid and alkaloid were mixed, evaporated to small bulk and water added to the precipitation point. On cooling small crystals separated, m. p. 194–196°. They could not be recrystallized from any single solvent. All the fractions obtained had the same rotation, and this was not altered by three precipitations of the first fraction.

Rotation. 0.1060 g. made up to 20 cc. with absolute methyl alcohol at 20° gave $\alpha_D = +1.25°$; $l = 2$; $[\alpha]_D$ +117.8°.

Anal. Calcd. for $C_{51}H_{52}O_6N_5Cl$: Cl, 4.1. Found: Cl, 4.26.

A 1-g. portion of the purified first fraction was decomposed with ammonia and the ammonium salt of the acid isolated. It gave a zero rotation.

Mono-quinine Salt.—This salt could not be recrystallized readily, but three fractions of microscopic, colorless crystals were obtained from benzene containing a little ethyl alcohol, m. p. 152–155". The fractions and the salt recovered from the mother liquor all gave the same rotation.

Rotation. 0.1060 g. made up to 20 cc. with absolute methyl alcohol at 20° gave α_D = –0.624'; $l = 2$; $[\alpha]_D$ –58.89'.

Anal. Calcd. for $C_{33}H_{32}O_6N_3Cl$: Cl, 6.13. Found: Cl, 5.91.

α-Phenyl-β-naphthoquinoline-γ-carboxylic Acid.—This was prepared and purified according to the method of Dobner and Kuntze[12] and was obtained in 50% yield, m. p. 290" (Dobner, 53% yield, m. p. 296°).

Anal. Calcd. for $C_{20}H_{13}NO_2$: neut. equiv., 299. Found: 299.3.

3-(2-Carboxyphenyl)-6-phenylpyridine 2,4-dicarboxylic Acid.—Dobner[12] reports that α-phenyl-β-naphthoquinoline-γ-carboxylic acid could not be oxidized to a tricarboxylic acid, while the corresponding α-naphthoquinoline compound was oxidized to the tricarboxylic acid with alkaline permanganate at 50°. Immerheiser[13] reported the oxidation of β-naphthoquinoline-8-sulfonic acid by dissolving the potassium salt of the acid in water and using a neutral solution of potassium permanganate at ordinary temperatures. It was found that by this latter method α-phenyl-β-naphthoquinoline-γ-carboxylic acid could be oxidized very rapidly at ordinary temperatures to the corresponding tricarboxylic acid, and by using a large excess of permanganate until a permanent purple color remained in the reaction mixture, no unoxidized material was ob-

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[12] Dobner and Kuntze, *Ann.*, 249, 129 (1889).

[13] Immerheiser, *Ber.*, 22, 405 (1889).

tained. No ketone acid was isolated corresponding to those reported by Immerheiser[11] and Dobner.[12]

A solution of 14.5 g. of α-phenyl-β-naphthoquinoline-γ-carboxylic acid in 600 cc. of warm water was treated with a concd. solution of potassium hydroxide until the resulting solution was just alkaline to phenolphthalein. The solution was cooled and placed in a 2-liter, 2-necked flask fitted with a mechanical stirrer and a dropping funnel. A concentrated aqueous solution of potassium permanganate (25 g., 20% excess) was added gradually with rapid stirring. The mixture warmed up considerably and the decolorization was instantaneous. The manganese dioxide was allowed to coagulate overnight, the clear solution decanted off, and the manganese dioxide extracted thoroughly with boiling water. The combined filtrates, on being made strongly acid to methyl orange with sulfuric acid, gave a white oily precipitate which did not crystallize on standing. This was extracted with ether and dried over anhydrous magnesium sulfate. On removal of the solvent, 16.5 g. of crystalline material was obtained, m. p. 123–129°. It was recrystallized by dissolving it in the minimum amount of hot ethyl acetate and adding ligroin to the point of precipitation. On cooling, 13 g. (74%) of small colorless crystals was obtained. Recrystallization from ethyl acetate gave a constant melting point of 202°.

Anal. Calcd. for $C_{20}H_{13}NO_6$: C, 66.1; H, 3.58; neut. equiv., 121. Found: C, 59.9; H, 3.32; neut. equiv., 122.7.

Alkaloid Salts of 3-(2-Carboxyphenyl)-6-phenylpyridine-2,4-dicarboxylic Acid

Mono-strychnine Salt.—The salt was made in methyl alcohol, and would not crystallize readily from any solvent. The crude material gave zero rotation with sodium light, and so did a small crystalline fraction obtained from a mixture of chloroform and ethyl acetate.

Di-strychnine Salt.—This separated in small, colorless prisms from benzene containing a little ethyl alcohol; m. p. about 238' with decomposition.

Anal. Calcd. for $C_{62}H_{57}O_{10}N_5$: neut. equiv., 344.3. Found: neut. equiv., 341.7.

A constant rotation was shown by all fractions; *rotation:* 0.2022 g. made up to 20 cc. with chloroform at 20° gave $\alpha_D = -0.173°$; $l = 2$; $[\alpha]_D -8.57"$.

The first fraction and the salt recovered from the mother liquors were both decomposed with ammonia and the ammonium salt isolated in the usual manner. Neither showed rotation.

Mono-brucine Salt.—This salt could not be recrystallized readily from any solvent. A few crystals were obtained from water, and they, as well as the crude material, gave zero rotation.

Di-brucine Salt.—The salt was crystallized from a small volume of absolute ethyl alcohol. It separated in small, regular prisms and all the fractions obtained showed no rotation. The salt had no definite melting point; it partially melted at 204° with decomposition, and was completely melted by 225°.

Anal. Calcd. for $C_{66}H_{65}O_{14}N_5$: neut. equiv., 383.6. Found: neut. equiv., 383.6.

Mono-cinchonine Salt.—The crude salt had a rotation of +75.46°.

Rotation. 0.2068 g. made up to 25 cc. with absolute methyl alcohol at 20° gave $\alpha_D = +1.249°$; $1 = 2$; $[\alpha]_D +75.46°$.

Four fractions were isolated by crystallization from water containing a little ethyl alcohol and none showed any change in rotation; the crystals melted and resolidified at 174–176°, and finally melted with further decomposition at 200–204°. The first fraction, after two recrystallizations rotated as follows: rotation, 0.2016 g. made up to 25 cc. with methyl alcohol at 20° gave $\alpha_D = -1.214°$; $l = 2$; $[\alpha]_D +75.26°$.

This fraction and the salt from the original mother liquor were decomposed and the ammonium salts isolated. Neither showed rotation.

Esters of 3-(2-Carboxyphenyl)-6-phenylpyridine-2,4-dicarboxylic Acid

It was thought that the ortho-substituted groups might be enlarged by esterification of the three acid groups with an alcohol of comparatively large size. If a crystalline tri-ester could be obtained, then resolution might be possible by forming salts of the pyridine nitrogen. Alternatively, a tri-ester of an optically active alcohol might separate into two diastereoisomers on recrystallization.

Tricarboxylic Acid Trichloride.—The acid was treated with an excess of thionyl chloride in a flask fitted with a ground-in water condenser until there was no further reaction. This required about two hours. The acid chloride was then washed out with ligroin and the latter decanted. The acid chloride was dried in a vacuum desiccator; m. p. 127–130°. It was found impossible to recrystallize it from any of the ordinary solvents.

Anal. Calcd. for $C_{20}H_{10}NO_3Cl_3$: Cl, 25.47. Found: Cl, 24.7.

Tri-*n*-butyl Ester of the Tricarboxylic Acid.—One mole of the acid trichloride was treated with 3 moles of *n*-butyl alcohol and warmed on the water-bath until the mass was homogeneous. The product was poured into water, made slightly alkaline with sodium carbonate and extracted with ether. The ethereal layer, after being washed with water and dried, gave a thick sirup which could not be crystallized.

Trimenthyl Ester of the Tricarboxylic Acid.—This was prepared in an analogous manner to the tributyl ester. The sirup so obtained could not be recrystallized.

Rotation. 0.2559 g. made up to 20 cc. with acetone at 20° gave $\alpha_D -0.97°$; $1 = 2$; $[\alpha]_D -38°$.

Summary

1. The possibilities of optical isomerism in the phenylpyridines as compared with the diphenyl series is discussed.
2. 10-Chloro-α-naphthoquinoline and 2-(2-carboxy-6-chlorophenyl)-pyridine-3-carboxylic acid were prepared. Salts of this acid with several alkaloids were made, but no separation into diastereoisomers was observed.
3. 3-(2-Carboxyphenyl)-6-phenylpyridine-2,4-dicarboxylic acid was prepared; its alkaloid salts appeared to exist in only one form.

URBANA, ILLINOIS

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

SYNTHESIS OF NERVONIC ACID

BY J. B. HALE, W. H. LYCAN AND ROGER ADAMS

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Klenk[1] isolated from cattle and human brains a cerebroside which upon hydrolysis gave galactose, sphingosin and an unsaturated acid melting at 41°. He established its formula as $C_{24}H_{46}O_2$ and its exact constitution as tetracosene-13-oic acid (I) by oxidizing it to pelargonic acid and tridecamethylene dicarboxylic acid. Moreover, on catalytic reduction it yielded a saturated acid melting at 85° identical with lignoceric acid from beechwood tar and with n-tetracosanic acid synthesized from behenic acid. He also reported that by melting over nitric acid, a new isomeric acid melting at 61° was obtained. Nervonic acid was shown to be identical with selachaleic acid isolated from whale oil.[2]

$$CH_3(CH_2)_7—CH{=}CH—(CH_2)_{13}—COOH \qquad (I)$$

It is obvious that nervonic acid is probably the cis form of erucylacetic acid. By synthesis this has been shown to be the case. Ethyl erucate was reduced to erucyl alcohol (II) which was converted to the bromide and this in turn carried through a malonic ester synthesis to erucylacetic acid (III):

$$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}—CH_2—OH \longrightarrow$$
$$\underset{\text{II}}{CH_3(CH_2)_7CH{=}CH(CH_2)_{11}—CH_2—CH(COOC_2H_5)_2} \longrightarrow$$
$$\underset{\text{III}}{CH_3(CH_2)_7CH{=}CH(CH_2)_{11}—CH_2CH_2COOH}$$

Several runs of product were made and only once was the yield essentially all acid melting at 39–40° (Klenk 41°). In general the product was a mixture of cis and trans isomers which could, however, be separated by crystallization, giving the low melting at 39–39.5° and the high melting at 61°. On account of the high boiling point of all the intermediates the tendency to isomerize to the stabler trans forms of the intermediates was probably increased.

The low-melting erucylacetic acid was readily converted to the high-melting form by melting over nitric acid and both forms were reduced to *n*-tetracosanoic acid identical with an authentic sample of this acid. Moreover, the mixed erucylacetic acids were esterified and reduced and gave a product melting at 55°, identical with that of ethyl tetracosanate made by a different method.

Experimental

Erucyl Alcohol.—To a mixture of 200 g. of methyl erucate (0.5 mole) and 2000 *cc.* of anhydrous n-butyl alcohol in a 5-liter flask equipped with a reflux condenser was added

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[1] Klenk, Z. *Physiol. Chem.*, 145, 244 (1925); 157, 283 (1926); 166, 268 (1927); 166, 287 (1927).

[2] Tsujimoto and Mitsumaru, Z. *deut. Öl. Fett.-Ind.*, 46, 385 (1926); J. *Soc. Chem. Ind. Japan* (*Suppl.*), 30, 868 (1927); Hilditch and Houlbrook, Analyst, 53, 246 (1928).

slowly 50 g. of sodium in large chunks. It was necessary to control the reaction occasionally with an ice jacket. When nearly all the sodium had been consumed, 80 cc. of water was added to the flask and the contents refluxed vigorously for half an hour. After partial cooling, 600 cc. more water was added, whereupon two layers separated. The lower layer was siphoned off and discarded and the upper layer was washed twice with 500-cc. portions of 20% sodium chloride solution. An aqueous solution of 25 g. of calcium chloride was added and the mixture subjected to steam distillation until removal of the butyl alcohol was complete. After cooling, the solid material was removed from the flask by hand, pressed between filter paper to remove as much water as possible and dissolved in two Liters of toluene by gentle heating. On cooling with tap water, a slush of calcium erucate separated out and was removed by filtration. The filtrate was separated from the small quantity of water that had been carried along and then the toluene removed by distillation. The crude product thus obtained was purified by distillation under diminished pressure; b. p. 200–205° at 1 mm. The yields varied up to 55% of the theoretical amount. A small sample of this product after several recrystallizations from petroleum ether melted at 34–35°. Willstätter and Mayer,[3] who have prepared erucyl alcohol by a somewhat similar method, record the melting point of their product as 34.5".

Erucyl Bromide.—A solution of 129 g. of erucyl alcohol (0.4 mole) in 400 cc. of anhydrous toluene was cooled to −10° in a 2-liter flask equipped with a mechanical stirrer, thermometer and dropping funnel. To this solution 40 g. of phosphorus tribromide (0.44 mole) in 200 cc. of anhydrous toluene was added, with stirring, at such a rate that the temperature never rose above −5°. The mixture was then heated on a steam-bath for four hours and the toluene removed by distillation. The product was dissolved in 500 cc. of ether, washed with two 100-cc. portions of a solution containing 10% potassium hydroxide and 10% sodium chloride and finally with water. The ether solution was dried with anhydrous magnesium sulfate, the ether removed and the product purified by distillation under diminished pressure. The yields were from 50–60% of the theoretical amount of erucyl bromide; b. p. 203–207° at 1 mm.

Erucyl Malonic Ester.—To a solution containing 4 g. of sodium dissolved in 104 cc. of absolute alcohol was added 33 g. of diethyl malonate (6 2 moles). Then 68 g. of erucyl bromide (0.175 mole) was run in slowly and the mixture refluxed with stirring for thirty-six hours, after which time it was only faintly alkaline to moist litmus paper. The alcohol was distilled off and 400 cc. of water containing about 3 cc. of hydrochloric acid was added. The product appeared on the surface as a brown oil which was separated from the rest of the mixture. This was dried by distilling from it 50 cc. of benzene. The yield of crude product thus obtained was 95 g.

It was found that the ester boiled above 270° at 1-mm. pressure so a high vacuum distillation system was arranged, This apparatus consisted of a high vacuum pump in connection with a mercury vapor pump which in turn was connected through all glass seals to a distilling flask and receiver. A liquid-air trap between the mercury vapor pump and the distilling flask prevented any fouling of the vacuum-producing system with volatile organic material. The pressure was recorded by means of a McLeod gage sealed in between the mercury vapor pump and the liquid-air trap. Bumping was prevented by inserting a small piece of clay plate into the liquid in the distilling flask before sealing it off. All low-boiling compounds were removed before placing the erucyl malonic ester in this system by heating to 220° first on a water pump and finally at 1 mm.-pressure on an oil-pump as long as any volatile material distilled. In this manner the product was found to boil at 203–207° at 0.001 mm. (It should be recorded that the pressure measured in this system was that existing between the mercury vapor pump

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[3] Willstatter and Mayer, *Ber.*, 41, 1478 (1928).

and the cold trap. The pressure on the ester itself may have been as high as 0.01 mm.) The yield of erucyl malonic ester was 62.5 g. (78%).

Anal. Subs., 0.2113: CO_2, 0.5400; H_2O, 0.1971. Calcd. for $C_{29}H_{54}O_4$: C, 74.68; H, 11.69. Found: C, 74.68; H, 11.99.

Erucylacetic Acid or Nervonic Acid.—The crude erucyl malonic ester obtained above was saponified without further purification.

A mixture of 95 g. of crude erucyl malonic ester, 56 g. of potassium hydroxide and 350 cc. of 60% alcohol was refluxed for forty-eight hours. The condenser was changed for downward distillation and after most of the alcohol had been removed, 500 cc. of water containing 60 g. of sulfuric acid was added. The resulting precipitate was extracted with several portions of ether, dried with anhydrous magnesium sulfate and filtered. After removal of the ether the product was heated at 175° for one hour to remove carbon dioxide, then distilled under diminished pressure. This distillation was carried out as rapidly as possible to minimize decomposition, and 40 g. of a product, b. p. 235–250° at 1 mm , was obtained. This was a mixture melting at 25–43° but was separated into three pure components by a scheme of fractional recrystallization as follows.

The entire 40 g. was dissolved in 300 cc. of absolute alcohol and cooled very slowly to −10°. The precipitate of fine white crystals was filtered and the mother liquor again cooled to −10°, when a second crop appeared which was filtered and added to the first. The combined product was then recrystallized twice more from 100-cc. portions of alcohol and a 10-g. yield of pure presumably *trans*-erucylacetic acid, m. p. 61°, was obtained. This corresponds to the trans form of nervonic acid, m. p. 61°, obtained by Klenk on melting the cis form over dilute nitric acid.

The original mother liquor was now evaporated on the steam-bath to about 76 cc. and cooled until a small precipitate of white crystals appeared, which were filtered without further cooling. A melting point indicated that this was a mixture of the cis and trans forms of the acid. On further cooling the mother liquor to −10° a generous crop of crystals separated which after drying melted at 36–38°. Two subsequent recrystallizations yielded 3 g. of a product, m. p. 39–39.5°; the melting point did not change after a third recrystallization. This corresponds to the nervonic acid of Klenk, m. p. 4041°.

Anal. Subs., 0.1668: CO_2, 0.4795; H_2O, 0.1886. Calcd. for $C_{24}H_{46}O_2$: C, 78.60; H, 12.64. Found: C, 78.39; H, 1265.

Further working of the mother liquor yielded only an oil which, although unidentified, was probably ethyl erucyl ether formed during the malonic ester condensation.

Conversion of the Cis Form of Erucylacetic Acid to the *Trans* Form.—A small sample of the cis nervonic acid, m. p. 39–39.5°, was melted over 15 cc. of dilute nitric acid, to which a pinch of sodium nitrite had been added. The product was separated by cooling and after two recrystallizations from absolute alcohol melted at 62–63'. A sample of this mixed with a sample of the trans form obtained before melted at 61–62°.

Anal. Calcd. for $C_{24}H_{46}O_2$: C, 78.60; H, 12.64. Found: C, 78.35; H, 12.59.

Reduction of Cis and *Trans* Forms of Nervonic Acid to n–Tetracosanoic Acid.—A sample of 0 2 g. of cis nervonic acid, m. p. 39–39.5°, was dissolved in 25 cc. of absolute alcohol, and the solution shaken with hydrogen under a pressure of 3 atm for one hour, in the presence of 0.1 g. of platinum oxide catalyst. The reduced acid separated as fine white crystals as the reduction proceeded. The product thus obtained after removal of the platinum was recrystallized three times from absolute alcohol, and three times from acetone. It then melted at 83–84°.

A sample of trans nervonic acid was reduced and the product purified according to the same procedure. This product also melted 83–84°, and a mixed melting point of the two acids showed no depression.

Anal. Calcd. for $C_{24}H_{48}O_2$: C, 78.17; H, 13.13. Found: C, 78.54; H, 13.29.

Various values have been recorded in the literature for the melting point of la-tetracosanoic acid. Levcne and Taylor,* who have synthetically prepared all the normal acids of this series, report 85–86° as the melting point of this member. Meyer, Brod and Soyka[5] obtained 85.5–86°, Brigl[6] 85°, and Levene, West, Allen and von der Scheer[7] 87.5–88°. Shriner, Nabenhauer and Anderson[8] obtained n-tetracosanoic acid from corn wax, and report as its melting point 85–86'. The last authors made mixed melting-point determinations with a sample of the same acid prepared by Taylor and Levene.[4] The acid prepared in this investigation melted at 83–84° and a mixed melting-point determination with a sample of Shriner's naturally occurring acid was made. It was found under the melting point conditions used that the melting point of the *n*-tetracosanoic acid, from reduction of erucylacetic acid, the natural n-tetracosanoic acid of Shrincr, Nabenhauer and Anderson and a mixture of the two was exactly the same, 83–84°. Recrystallization from various solvents failed to alter the melting point of either acid.

Ethyl Erucylacetate.—The ethyl ester of erucylacetic acid was prepared by refluxing 110 g. of the acid (0.3 mole) (which was presumably a mixture of the cis and trans isomers) with 1 liter of absolute alcohol to which 2 cc. of concentrated sulfuric acid had been added, overnight. The product boiled at 233–234° at 1 mm., and the yield was 117 g.

Anal. Subs., 0.1553: CO_2, 0.4489; H_2O, 0.1774. Calcd. for $C_{26}H_{50}O_2$: C, 79.11; H, 12.77. Found: C, 78.83; H, 12.79.

Ethyl *n*-Tetracosanoate.—A solution of 5 g. of ethyl erucylacetate in 100 cc of 95% alcohol was shaken with hydrogen under 2.5–3 atmospheres' pressure, in the presence of 0.2 g. of platinum oxide catalyst. The reduction required only a few minutes and the product crystallized out as it was formed. The pressure was released and the alcohol heated to boiling to take the ester back into solution. The hot solution was filtered free from platinum and cooled again. The white plates which crystallized out were filtered and recrystallized three times from ethyl alcohol and four times from acetone; m. p. 55–56' (corr.). Lcvene and Taylor[4] record the melting point of the same compound prepared by esterifying the ester as 55.5–56.5°.

Summary

Erucylacetic acid has been prepared from erucyl alcohol through the bromide and malonic ester synthesis and has been shown to be identical. with nervonic acid obtained from hydrolysis of the cerebroside isolated from human brains.

URBANA, ILLINOIS

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[4] Levene and Taylor, J. *Biol.* Chem., ***59***, 905 (1924).

[5] Meyer, Brod and Soyka, *Monatsh.*, 34, 113 (1913).

[6] Brigl, Z. *physik.* Chem., ***95***, 161 (1925).

[7] Levene, West, Allen and von der Scheer, *J.* Biol. *Chem.*, 23, 71 (1915).

[8] Shriner, Nabenhauer and Anderson, THIS JOURNAL. 49, 1290 (1927).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PYROLYSIS OF ALLENE AND METHYLACETYLENE[1]

BY RICHARD N. MEINERT[2] AND CHARLES D. HURD[3]

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Prior to this work, no record exists concerning the behavior of methylacetylene, $CH_3—C≡CH$, at high temperatures. Except for Lebedev's work, the same may be said for allene, $CH_2=C=CH_2$. Lebedev[4] heated allene at 140° under pressure for several days and obtained a series of polymers. He also subjected trimethylallene, sym- and *unsym*-dimethylallene to the same conditions of warmth, pressure and time and found that they also gave rise to polymers.

General Results with Allene

The present experiments were made over a temperature range of 400 to 600° and the hot contact time was made a matter of seconds rather than a matter of hours and days as in Lebedev's experiments. Here, also, it was found that polymerization was the predominant reaction of allene. At a temperature of 500° and with a contact time of eighty-six seconds, four-fifths of the allene entering the reaction tube was consumed and 90% of the product appeared as liquids. These liquid products were distilled repeatedly so as to obtain pure fractions. The properties of the lower-boiling fractions were found to be very nearly identical in physical constants and general appearance with two of Lebedev's polymers, namely, the dimer and the alpha tetramer. The higher-boiling fractions differed from Lebedev's polymers but were high-boiling tarry substances. Lebedev stated that several of the polymers, in particular the trimer and the beta tetramer, were unstable at elevated temperatures, so it is not surprising that they were not encountered in the present experiments.

A temperature of 500" seems to be the best for the formation of these liquids by the flow method. At lower temperatures, the reaction proceeds too slowly, while at higher temperatures less polymeric liquids and more gaseous products are formed although the percentage of allene pyrolyzed is greater. Thus, at 600°, with a hot contact time of fifty seconds, only 43%

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[1] This paper contains results obtained in an investigation on "The 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] American Petroleum Institute Junior Research Fellow.

[3] Director, Project No. 18.

[4] Lebedev, J. *Russ. Phys.-Chem. Soc.*, *45*, **1249–1388 (1913); J.** *Chem. Soc.* (abst.). **104, 1285 (1913).**

of the non-recoverable allene appeared as liquids. Concurrently, each 10 cc. (gaseous) of this allene gave rise to about four cc. of gas. At 500°, with a hot contact time of eighty-six seconds, nine-tenths of the non-recoverable allene was changed into liquids and only 1 cc. of gas was formed from each 10 cc. of allene. Carbon and tar formation played a major role in the 600° experiments, whereas at 500° almost no tar or carbon was formed.

The gases formed in the pyrolysis of allene were methane, hydrogen, ethane, ethylene and small amounts of acetylenes. Methane represented the larger part at 500°, but at 600° the volumes of methane and hydrogen were almost equal. In all cases, however, the gases represented but a small part of the reaction products.

Mechanism of the Pyrolysis.—Earlier studies on the behavior of butane, isobutane[5] and isobutylene[6] at high temperatures furnish a basis with which to predict something of the mechanism of allene pyrolysis. The butanes, having no double bonds in their structure, change exclusively into compounds of simpler structure, evidently by complete rupture of C–C or C–H bonds. Isobutylene, with one double bond and one single bond, gives rise not only to simpler compounds but also to more complex ones. The simpler compounds appear to be formed by single bond C–C scission, whereas the complex liquid hydrocarbons are formed because of double bond C=C activation which is followed by a polymerization process. Allene presents no opportunity to break into simpler compounds by scission of single bonds since only double bonds are present in the allene chain. Therefore, it would be logical to assume that only complex liquid polymerization products should be formed on pyrolysis. As has been shown, this is indeed the major, and nearly the exclusive, primary effect. It may be symbolized as follows

$$x\ CH_2{=}C{=}CH_2 \longrightarrow x\ [\underset{|}{C}H_2{-}\underset{|}{C}H{=}CH_2] \longrightarrow (C_3H_4)_x$$

Probably, as Lebedev suggested, these polymers are cyclobutane derivatives, the dimer being dimethenylcyclobutane. This dimer, with two double bonds still in its structure, may undergo further polymerization reactions.

General Results with Methylacetylene.—Methylacetylene which contained about 5% of allene as an impurity was prepared by the action of alcoholic potassium hydroxide on propylene bromide. This was used in the first experiments. As in the case of allene, liquids were by far the most abundant product of the pyrolytic reaction. With a hot contact time of one hundred seconds at 500° the liquids accounted for 78% of the methylacetylene pyrolyzed, while at 575° and forty-eight seconds the percentage

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[5] Hurd and Spence, THIS JOURNAL, 51, 3353 (1929).

[6] Hurd and Spence, *ibid.*, 51, 3501 (1929).

of liquids rose to 88. At 650° there was a great increase in the amount of ethylene, hydrogen and methane formed, while the yield of liquids dropped to 61%. This behavior paralleled that of allene under similar conditions. Furthermore, when these liquid products were fractionally distilled as carefully as the small amounts available would permit, the fractions were found to be very nearly identical with the lower-boiling allene polymers. There was no trace of the formation of any aromatic hydrocarbons.

When the off-gas which resulted from the pyrolysis of methylacetylene was analyzed, there was always a considerable portion which was gradually absorbed in 82.4% sulfuric acid. This portion might represent either allene or propylene. Aside from the fact that some allene was a contaminant in the original methylacetylene, the reasons for thinking that it was allene are as follows: (1) because of its slow rate of solution; (2) because propylene could not have been formed except by hydrogenation, an improbability in view of the small concentration of hydrogen in the off-gas; (3) because the liquid products were so very similar to those obtained from pure allene. To settle the point definitely, however, it was deaded to pyrolyze an allene-free specimen of methylacetylene and to identify the off-gas in question as bromides. Propylene would give its dibromide, whereas allene would give rise to its di- and tetrabromides, the latter of which would be recognized by its lachrymatory properties, its high boiling point and its comparatively high melting point.

Accordingly, some pure methylacetylene was prepared by the interaction of sodium acetylide and either methyl iodide or dimethyl sulfate. The use of dimethyl sulfate, which is a new method, is preferable. This methylacetylene was pyrolyzed at 500°. The off-gas was carefully collected and all acetylenes were extracted from it by alkaline potassium iodomercurate reagent. The gas which remained was passed several times through a solution of bromine in carbon tetrachloride so as to form bromides of all unsaturated hydrocarbons still remaining. On fractionation these bromides were found to consist principally of allene dibromide and allene tetrabromide. This proves that allene was formed during the pyrolysis of methylacetylene. The similarity of the liquids obtained from methylacetylene to those obtained from allene suggests that these liquids are formed from allene, rather than directly from methylacetylene.

Theoretical Considerations

Acetylene, when heated, undergoes pyrolysis to a large extent into benzene[1] and other aromatic hydrocarbons. Analogously, one might assume that methylacetylene should change into mesitylene and other aromatics. Such, however, is not the case. The fundamental change in methylacetylene is one of isomerism into allene, a change which is predictable on the

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[1] Pease, THIS JOURNAL, 51, 3470 (1929).

basis of the "three carbon system."[8] If E represents any such element as C, N or O, the expression: $H—E—E{=}E' \rightleftarrows E{=}E—E'—H$ represents a general formulation of this type of rearrangement. Familiar cases of this type are keto–enol, nitroso to oxime, and the three-carbon system.

With a triple bond in the chain rather than a double bond, similar mobility of hydrogen exists: $H—E—E{\equiv}E \rightleftarrows E{=}E{=}E—H$. Because of its similarity to the keto–enol isomerism, the name "keteno-ynol" is suggested for this type of change. Some well-known illustrative cases are HOCN and HNCO, $C_6H_5CH_2—CN$ and $C_6H_5CH{=}C{=}NH$, $H_2N—CN$ and $HN{=}C{=}NH$, ketene and hydroxyacetylene. Methylacetylene and allene also fit into this scheme: $H_3C—C{\equiv}CH \rightleftarrows H_2C{=}C{=}CH_2$. Allene may be converted into its isomer by the action of sodium. The reverse reaction is the pyrolysis of methylacetylene. It is interesting to point out that all the "keteno" structures mentioned above are the forms into which the "ynol" isomers change at high temperatures. No doubt this is associated with the fact that the former represent more symmetrical structures.

Experimental Part

Apparatus.—The flow method was used. The gaseous hydrocarbon was stored in a gasometer of 57-liter capacity, in an 8-liter bottle, or in a closed steel cylinder under pressure. The gas was passed from its container through a wet test meter, thence through two drying towers, a flowmeter of the capillary type, a calcium chloride tube, and then it was conducted into the reaction tube. The tube was of pyrex glass 2.5 cm. in diameter and was heated over 76 cm. of its length by an electric tube furnace. The volume of the tube within the furnace limits, after deduction of the volume of the thermocouple sheath, was 290 cc. The furnace was supported in a vertical position so that any liquids formed in the reaction could be removed from the tube by gravity. The effluent gases were passed through a trap at 0° which was placed directly beneath the furnace. This trap served to collect the liquid products.

The temperature of the furnace was measured and automatically controlled by a Leeds–Northrup potentiometer type recorder-controller. A chromel-alumel thermocouple was used, and it was protected by a thin pyrex sheath which was placed directly within the reaction tube.

The gases were analyzed in the manner previously outlined by Hurd and Spence.[9]

Preparation of Allene and Methylacetylene.—Allene was prepared from dibromo-2,3-propene-1, as outlined by Hurd, Meinert and Spence.[10] The gas was washed and stored in a gasometer over saturated sodium chloride solution.

Methylacetylene, contaminated with about 5% of allene, was prepared from propylene bromide and hot alcoholic potassium hydroxide solution. This preparation, and also the preparation of pure methylacetylene from methyl iodide and sodium acetylide, is given in detail in the same reference.[11] The methylacetylene, after purification, was liquefied and stored in a small steel gas cylinder.

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[8] For a discussion of recent work on this subject, see "Annual Reports on the Progress of Chemistry," 25, 119–130 (1929).

[9] Hurd and Spence, THIS JOURNAL, 51,3356–3357 (1929).

[10] Hurd, Meinert and Spence, *ibid.*, 52,1143 (1930).

[11] Ref. 10, p. 1141.

Methylacetylene from Dimethyl Sulfate.—A one-liter, 3-necked flask was fitted with a mercury-sealed stirrer, an exit tube, and a wide-mouthed inlet tube which reached nearly to the bottom of the flask. After replacing air in the flask with dry hydrogen, 36 g. of sodium was inserted, the flask cooled to −60° with a bath of acetone and solid carbon dioxide, and then dry ammonia was condensed in the flask. The stirrer was started as soon as a little ammonia had condensed. In all, about 500 cc. of liquid ammonia was required. When the sodium had dissolved, the stream of ammonia was detached and a current of acetylene was passed into the well-stirred mixture. When all of the sodium-blue color had disappeared due to the formation of colorless sodium acetylide, the current of acetylene was stopped, and a dropping funnel was inserted to replace the stirrer. The top of the funnel was connected with a tube to the reaction flask, the tube serving as a pressure equalizer.

The exit tube was connected to a gas washing train consisting of a Wolff bottle with water, another with 10% sulfuric acid, and a calcium chloride drying tower. Bunsen valves were inserted between the two wash bottles and between the reaction flask and the first wash bottle. From the drying tower a connection led to a spiral glass condenser with receiver attached, which was immersed in a Dewar flask and maintained at −78°. The methylacetylene condensed therein.

Two hundred grams of dimethyl sulfate was added very slowly into the reaction flask from the dropping funnel, keeping the Bask at −60°. As each drop fell there was a rush of gas from the exit tube. This necessitated careful control during the addition of the reagent. Most of the methylacetylene had passed over into the condenser by the time the last of the dimethyl sulfate was added. Then the reaction flask was allowed to warm up to drive over the remainder of the product. The methylacetylene was distilled from a large test-tube, using the Davis spiral, vacuum-jacketed column. The yield and the ease of manipulation were about the same with dimethyl sulfate as with methyl iodide. The relative cheapness of the former, however, is greatly in its favor.

The boiling point of the methylacetylene was found[12] to be −23". Since this differs from the literature value of −27.5°, the accurate vapor pressure of methylacetylene has been studied in considerable detail by Professor G. B. Heisig of the University of Minnesota. This will be published separately.

Products Obtained from the Pyrolysis of Allene.—The data for the pyrolysis of allene are given in Table I.

These data show clearly that when allene was pyrolyzed, most of it was converted into liquids. As would be expected, the conversion was more

TABLE I

PRODUCTS OBTAINED FROM THE PYROLYSIS OF ALLENE

Run number	1	2	3	4	5
Temperature, °C.	500	400	450	600	500
Contact time, seconds	54.7	60.8	52.0	50	86
Entering flow, cc./min.	111	115	126	108	69
Exit flow, cc./min.	45	102	93	62	23
Pressure in tube, mm.	754	754	754	753	730
Vol. entering gas, liters	4.79	3.34	3.59	2.37	13.05
Vol. exit gas, liters	1.96	2.97	2.64	1.35	4.30
Allene in entering gas, %	96.0	92.9	92.9	95.8	93.0

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[12] For assistance in the purification of the methylacetylene we are indebted to Mr. Forrest Pilgrim.

TABLE I (*Concluded*)

Composition of exit gas, percentage by volume					
Acetylenes	2.5	0.9	0.7	1.0	5.0
Allene	79.7	89.8	89.5	28.0	52.7
Ethylene	2.3	....		10.6	4.3
Hydrogen	1.4	....	....	21.3	6.2
Paraffins, C_nH_{2n+2}	4.9	....	....	23.8	14.2
n equivalent to	1.82	....	....	1.10	1.47
CO and CO_2	1.1	...		0.7	1.1
Nitrogen	7.2	...	....	13.4	13.2
Extent of pyrolysis, %	66.2	13.8	28.8	83.5	80.5
Gaseous products formed per liter of allene entering, cc.					
Acetylenes	11.9	....	....	0	18.5
Ethylene	11.9	....	....	65	15.3
Hydrogen	5.9	....	...	130	21.8
Paraffins	20.2	....	....	146	50.9
Gaseous products formed per liter of allene pyrolyzed, cc.					
Acetylenes	18	....	....	0	23
Ethylene	18	....	....	78	19
Hydrogen	9	....	....	156	27
Paraffins	32	....	....	175	63
Liquid products, wt. in g.	....	0.24	1.29	1.41	15.8
Percentage yield of liquids, on basis of allene pyrolyzed	....	32	75	43	90

nearly complete when the gas was heated for a longer time and when the temperature was between 500 and 600°. A comparison of Runs 2, 3, 1 and 4, all of which had similar contact times, shows the increasing percentage of decomposition of allene with the increase in temperature. A comparison of Runs 1 and 4 shows that at 600° about five times the volume of gases was formed as was noticed at 500°, while the percentage of liquids was considerably less. It should be stated that the deposit of carbon and viscous tarry matter in the tube was quite considerable at 600° and almost negligible at 500". Comparison of Runs 1 and 5 shows that if the allene was heated for a longer time, the amount of gaseous products increased. This suggests that a large part of the gases is formed by the decomposition of the allene polymers if the reaction is carried out at 600°, or for too long a time at 500°.

The Liquid Products from **Allene.**—The 15.8 g. of liquids formed in Run 5 was fractionally distilled, taking care to obtain cuts as nearly pure as possible. The refractive index of each fraction was determined. In Table II the physical properties of these liquids are compared with similar data as given by Lebedev.[4] The properties in question are boiling point, odor, refractive index and general appearance.

A comparison of Fraction I with Lebedev's dimer and Fractions II and III with his α-tetramer shows that they possess similar properties. Lebe-

TABLE II

PROPERTIES OF ALLENE POLYMERS

	Fractions from allene at 500°	**Lebedev's polymers**
I	B. p. 63–66°; n_D^{20} 1.4358 Sharp, irritating odor; 1.2 g.	Dimer, b. p. 63–65°; n_D^{20} 1.42317 Sharp odor
II	B. p. 35–50° (10 mm.); n_D^{20} 1.5002 Turpentine odor; 2.9 g.	Trimer, b. p. 135°; n_D^{20} 1.49064
III	B. p. 71–80° (10 mm.); n_D^{20} 1.5142 Turpentine odor; 0.8 g.	α-Tetramer, b. p. 72–74° (9 mm.) Turpentine odor; n_D^{20} 1.50501
IV	B. p. 80–105° (10 mm.); n_D^{20} 1.5617 Kerosene odor; 1.2 g.	β-Tetramer, b. p. 101° (10 mm.) Kerosene odor; n_D^{20} 1.52624
V	B. p. 105–155° (8 mm.); 1.3 g.; n_D^{20} 1.596	
VI	B. p. 160–190° (10 mm.); 1.5 g.; n_D^{20} 1.63; very viscous; odor of burnt rubber	

dev stated that only the dimer and the α-tetramer were stable at elevated temperatures. Therefore, in our polymerization at 500°, one would not expect to find much of the other polymers as they tend to form tarry material. The first four fractions all gave a test for unsaturation with bromine.

Pyrolysis of Methylacetylene.—The data for the pyrolysis of methylacetylene which contained 5% of allene as impurity are given in Table III.

TABLE III

PRODUCTS OF THE PYROLYSIS OF METHYLACETYLENE

Run number	1	3	5	2	4
Temperature, °C.	500	500	550	575	650
Contact time, seconds	100	42	76	48	30
Entering flow, cc./min.	59	141	72.6	112	164
Exit flow, cc./min.	45	128	44.2	63	136
Pressure in tube, mm.	750	750	750	750	750
Vol. entering gas, liters	4.84	3.97	13.05	6.73	2.13
Volume exit gas, liters	3.69	3.60	7.92	3.77	1.76
Composition of entering gas					
Methylacetylene. %	95.9	95.0	95.6	95.0	95.0
Allene, %	4.1	5.0	4.4	5.0	5.0
Composition of exit gases, percentage by volume					
Acetylenes	83.7	88.0	52.0	48.0	14.0
Allene[a]	4.4	4.6	18.6	16.8	11.8
Ethylene	1.5	....	3.6	3.0	23.1
Hydrogen	0.2	....	6.8	5.9	18.9
Paraffins, C_nH_{2n+2}	....	....	11.6	....	27.6
n equivalent to	....	....	1.34	....	1.17
Extent of pyrolysis; %	27.4	10.6	64.5	67	87
Gaseous products formed per liter of methylacetylene entering, cc.					
Allene[a]	....	....	124	107	109
Ethylene	....	....	24.6	19	214
Hydrogen	....	....	46.4	38	175
Paraffins	....	....	79.1	...	255

TABLE III (*Concluded*)

Gaseous products formed per liter of methylacetylene pyrolyzed, cc.					
Allene[a]	...	....	192	159	125
Ethylene	....	....	37.1	28.5	246
Hydrogen	...	....	72.0	57.0	201
Paraffins	....	....	123.0	....	294
Liquid products, wt. in g.	1.8	...	12.6	6.3	8.1
Percentage yield of liquids, on basis of methylacetylene pyrolyzed	78.0	....	58.8	88.0	61.0

[a] "Allene" represents the gases dissolved in 82.5% sulfuric acid; it may contain propylene, but later work has shown that allene is the chief if not the exclusive product.

In Runs 1 and 3 the gaseous products formed were of such a small volume that a complete analysis was not made. In making the calculations it was assumed that the small amount of allene present in the entering gas was polymerized for the most part, inasmuch as the work on allene showed this to be the case at temperatures above 500°. In addition to the gaseous and liquid products, there was a considerable amount of carbon and some very viscid tarry material which was deposited on the walls of the reaction tube. At the higher temperatures, this deposit became so great as to nearly clog the exit of the reaction tube.

Liquid Products from Methylacetylene.—The comparatively small volume of liquids which were obtained from methylacetylene made it impossible to carry the fractionation as far as was done in the case of the allene polymers. However, they were fractionated and the boiling points and refractive indices taken. These data are listed in Table IV.

TABLE IV

PROPERTIES OF THE LIQUID PRODUCTS FROM METHYLACETYLENE

Run number	2			5		
Temperature	575°			550°		
Contact time	48 sec.			76.3 sec.		
Fraction	B. p., °C.	n^{20}_D	Odor	B. p., °C.	n^{20}_D	Odor
I	60–90	1.4780	Sharp	30–70	1.4602	Sharp
II	90–150	1.4990	Turpentine	35–60 (10 mm.)	1.4995	Turpentine
III	150–215	1.5320	......	60–85 (10 mm.)	1.537	Burnt rubber

The properties of the lower-boiling fractions greatly resembled the properties of the low-boiling allene polymers. The liquid fractions were distinctly not aromatic in type. They all decolorized bromine in carbon tetrachloride. Nor did they form any nitro derivatives when they were treated with a nitrating mixture of nitric and sulfuric acids. There was no evidence of any pure compound in quantity since the boiling point ascended steadily during the distillation. An examination of the boiling point and refractive index data shows that they lie outside of the range of the aromatic compounds. Considering the evident impurity of the methylacetylene liquid fractions, it is apparent that they lie within the range of the corresponding data from allene liquid fractions (compare Tables II and IV). This, together with the very strong resemblance which they have to the allene liquids in odor and general appearance, indicates that these liquids also consisted mostly of polymers of the same nature as those obtained from allene. The presence of considerable amounts of allene in the off gas shows that these liquids were probably formed from allene, which in turn was formed by an isomerization of the methylacetylene.

The Pyrolysis of Pure Methylacetylene.—Table V gives the data for this experiment, and includes the analysis of the entering gas and the exit gases.

TABLE V

PYROLYSIS OF PURE METHYLACETYLENE

Temperature, °C.	555"	Exit volume, cc.	3380
Contact time, seconds	74.5	Pressure in tube	740 mm.
Entrance flow	95.7 cc./min.	Extent of pyrolysis	71%
Entrance volume, cc.	6320	Liquids formed	3 g.

Gas analysis, % by volume

	Entrance gas	*Exit gas*
Carbon dioxide	0.0	0.6
Methylacetylene	95.7	46.1
Gas absorbed by 62.5% H_2SO_4	0.0	1.5
Gas absorbed by 82.4% H_2SO_4	.0	24.3
Ethylene	.0	2.2
Hydrogen	.0	2.2
Carbon monoxide	.0	1.0
Oxygen	.6	1.5
Paraffins, C_nH_{2n+2}	.0	9.7
n equivalent to	..	1.67
Nitrogen	3 4	10.9

Since 82.4% sulfuric acid dissolves both allene and propylene, it was decided to remove the acetylenes from the gas and to convert the remaining unsaturated hydrocarbons into their bromide derivatives. Differentiation between olefin dibromides and diene tetrabromides would then be fairly simple.

The off gas from the run (Table V) was passed from its storage bottle into a bottle filled with potassium iodomercurate solution in order to remove all of the unchanged methylacetylene. The bottle was shaken from time to time and finally allowed to stand overnight. The volume became constant, indicating complete removal of all acetylenes. The original volume of gas was 3300 cc., and the volume after removal of acetylenes was 1700 cc. The volume of acetylenes in the original gas, based on the gas analysis was 1518 cc., so it was certain that all acetylenes were taken out. The residual gas was then dried and passed into a solution of bromine'in carbon tetrachloride. The unbrominated gas was collected and passed again through the bromine solution, and the apparatus was flushed out with a liter of air.

The bromides in the brominating bottle were then worked up. Their volume was 2 cc.; refractive index 1.533; initial boiling point, 140°. The liquid did not solidify at −75°. This 2 cc. of bromides was separated into two very small fractions by distillation at 9 mm. The boiling points could not be determined accurately due to the small amount of material distilled, but that of the first fraction was between 60 and 90°. Its refractive index was 1.523 and it did not solidify at −75°. The higher-boiling fraction which remained in the distilling flask had a refractive index of 1.582. It solidified at −20° in an ice–salt mixture. It began to melt at −5° and melted over a considerable range, indicating that it was not pure. This fraction of the bromides had an odor like that of allene tetrabromide and it had the powerful lachrymatory properties which are characteristic of allene tetrabromide.

The results provide satisfactory evidence that the portion of unsaturated hydrocarbons which were removed in the 82.4% sulfuric acid during the gas analysis consisted of allene. The bromides were evidently a mixture of allene dibromide and allene tetrabromide. Previous experience in brominating allene has shown that there is always some allene dibromide formed which is difficult to convert to the tetrabromide. The fact that highly purified allene tetrabromide solidifies in a salt–ice mixture[13] and melts at 10.7°, while the impure bromide obtained in this experiment also solidified and melted in the range of −5 to 0°, is a satisfactory proof of the identity of the latter. That the refractive index, 1.582, is lower than that of pure allene tetrabromide, 1.6206, is not surprising in view of the evident impurity of the former. Some of the dibromide undoubtedly remained in the tetrabromide residue. To obtain allene tetrabromide of high purity, it has been shown[13] that fairly large quantities, enabling several crystallizations, are essential.

Summary

In the pyrolysis of allene, it has been shown that the predominant reaction is a polymerization to form a dimer, a tetramer and higher polymers. There is no evidence of the formation of aromatic hydrocarbons.

The pyrolysis of methylacetylene has also been investigated. Evidence is offered to show that it first isomerizes to allene, which then polymerizes in its customary manner. The relationship of methylacetylene to the "three-carbon system" has been developed, and the classification of allene and methylacetylene as of the keteno-ynol type has been suggested.

A method for the preparation of methylacetylene from dimethyl sulfate and sodium acetylide has been given.

EVANSTON, ILLINOIS

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[13] Hurd, Meinert and Spence, THIS JOURNAL, 52, 1145 (1930).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF QUEEN'S UNIVERSITY]

THE PREPARATION OF 1-NAPHTHOIC NITRILE FROM 1-NAPHTHYLAMINE

BY JOHN A. MCRAE

RECEIVED AUGUST 22, 1930 PUBLISHED NOVEMBER 5, 1930

In summing up their results on the preparation of 1-naphthoic nitrile by various methods, Whitmore and Fox[1] stated recently that "treatment of 1-naphthylamine by the Sandmeyer reaction gave none of the nitrile." This statement is surprising in itself and is contrary to previous authors to whose work Whitmore and Fox make no reference. Thus, Bamberger and Philp[2] reported that the Sandmeyer reaction is a good method for the preparation of 1-naphthoic nitrile and Richter[3] commented favorably on the same method. Clarke and Read,[4] using their modification of the usual Sandmeyer process, obtained a yield of 55% of 1-naphthoic nitrile. It was thought of interest to test the validity of Whitmore and Fox's results and accordingly a study of the preparation of 1-naphthoic nitrile has been carried out, principally as a student's exercise, in the course of which various methods used in well-known laboratory textbooks (Gattermann, Cohen, Henle, Fisher) for preparing *p*-toluic nitrile from *p*-toluidine have been employed as a basis, as well as the important improvements described by Clarke and Read and the interesting process of Korczynski[5] in which potassium nickel cyanide is substituted for potassium cuprocyanide but which had not been applied hitherto to diazotized 1-naphthylamine.

In agreement with earlier work no difficulty has been encountered in obtaining 1-naphthoic nitrile from 1-naphthylamine by the Sandmeyer reaction, the yields varying from 25 to 35%. We were unable to increase the yield beyond 35% but on the other hand we did not discover conditions under which no naphthoic nitrile was produced. The Korczynski method did not give sensibly greater yields than the ordinary Sandmeyer process but by adding the acid diazo solution to potassium nickel cyanide containing sufficient alkali to neutralize the free acid of the diazo solution, the nitrile has been produced repeatedly in yields of 58 to 65%.

My thanks are due to Messrs. F. S. Wilder and J. W. McCutcheon for their assistance in carrying out most of the experimental work.

Experimental

Preparation of 1-Naphthoic Nitrile from 1-Naphthylamine

(a) Using Potassium Nickel Cyanide.—1-Naphthylamine was diazotized by dis-

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[1] Whitmore and Fox, THIS JOURNAL, 51, 3363 (1929).

[2] Bamberger and Philp, *Ber.*, 20, 241 (1887).

[3] Richter, *ibid.*, 22, 2449 (1889).

[4] Clarke and Read, THIS JOURNAL, 46, 1001 (1924).

[5] Korczynski, Mrozinski and Vielau, *Compt. rend.*, 171, 182 (1920); Korczynski and Fandrich, *ibid.*, 183, 421 (1926).

solving the amine (28.6 g. = 1/5 mole) in 600 cc. of hot water and 20 cc. of concentrated hydrochloric acid. With vigorous mechanical stirring the solution was cooled to 0° and maintained at that temperature during the addition first of 50 cc. of concentrated hydrochloric acid and then of a solution of 14.4 g. of sodium nitrite in 60 cc. of water. Any slight excess of nitrous acid was destroyed by the addition of urea.

The cyanide solution was made by adding a solution of 72.7 g. of a good grade of nickel nitrate in 100 cc. of water to a solution (250 cc.) containing 81.4 *g.* of potassium cyanide and 20 g. of sodium hydroxide. The cyanide solution, contained in a 5-liter flask, was mixed with 150 cc. of benzene and some crushed ice and vigorously stirred while the diazo solution was added during the course of one-half hour. The stirring was continued for another half hour while the temperature was maintained throughout at 0–5° and for a further two hours while the mixture was allowed to come to room temperature. It was then heated to 50°, cooled and the aqueous layer removed. The residual benzene solution was steam distilled until 5 liters was collected. The benzene which came off was used to collect the nitrile from the distillate. The benzene extract was washed with caustic soda, dried and after removal of the benzene the residue was fractionated under reduced pressure. Redistillation of the first fraction obtained boiling at 120–200° (20 mm.) gave 17.8 g. of 1-naphthoic nitrile, b. p. 165–170° (20 mm.), which quickly solidified.

The purity of the nitrile was confirmed by hydrolysis to 1-naphthoic acid, the yield being almost quantitative. No difficulty was experienced in obtaining pure 1-naphthoic acid of m. p. 161° by distillation of the crude acid under reduced pressure, b. p. 229–231° (50 mm.), and recrystallization of the distilled acid from toluene. This obviated the more lengthy purification of the acid by conversion into the ethyl ester followed by purification and hydrolysis of the ester which Whitmore and Fox found necessary.

(b) Using Potassium Cuprocyanide.—1-Naphthylamine was diazotized as described above in preference to diazotization in more concentrated solution corresponding with the laboratory directions given for *p*-toluidine by Fisher[6] and with that and the further exception that after steam distillation the nitrile was isolated as described above, the diazotized amine was converted into the nitrile according to Fisher's directions for p-toluic nitrile. Eight experiments using each time 28.6 g of amine gave an average yield of 27%. Steam distillation under reduced pressure of the crude product recommended by Clarke and Read[4] did not increase the yield appreciably. The addition of sodium carbonate to the diazotized naphthylamine seemed to result always in considerable decomposition and to avoid this the acidic diazo solution in several experiments was poured into potassium cuprocyanide solution containing alkali sufficient to neutralize the free acid of the diazo solution as used above with potassium nickel cyanide and as described by Henle[7] for p-toluic nitrile but without more favorable results. Increasing the ratio of potassium cyanide to correspond with $K_3Cu(CN)_4$ gave no better results. To avoid the lengthy steam distillation, extraction of the reaction mixture with ether–benzene was tried but the separation of the extracting liquid is poor and tedious. However, a yield of 26% of the nitrile was obtained from the extract. Addition of the acidic diazo solution to cuprocyanide solution made from potassium cyanide and copper sulfate as described in many laboratory manuals gave similar results.

1-Naphthoic acid may be obtained directly from the crude reaction mixture. The tar which separates in the absence of benzene or after the benzene is removed hardens on cooling and may be collected easily. The tarry residue from treatment of 28.6 g. of 1-naphthylamine was heated for seven hours under a reflux with 100 cc. each of sulfuric

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[6] Fisher, "Laboratory Manual of Organic Chemistry," 2d ed., p. 187.

[7] Henle, "Anleitung fur das organisch-chemische Praktikum," Zweite Auflage. p. 120.

acid, acetic acid and water—the hydrolyzing mixture used by Whitmore and Fox. The mixture was poured into water and from the solid which separated the 1-naphthoic acid was extracted with dilute ammonia. After precipitation from its ammoniacal solution, the crude naphthoic acid was purified as described above. The yields obtained were from *20–25%* of the calculated.

Summary

1. Contrary to a recent statement, 1-naphthoic nitrile is produced readily from 1-naphthylamine by the Sandmeyer reaction.
2. Very good yields of this nitrile can be obtained by a slight modification of the Korczynski method.

KINGSTON, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE CHEMICAL BEHAVIOR OF SOME BENZENOID HYDROCARBONS IN THE TESLA DISCHARGE

BY JAMES BLISS AUSTIN[1] AND IAN ARMSTRONG BLACK[2]

RECEIVED AUGUST 22, 1930 PUBLISHED NOVEMBER 5, 1930

Several years ago, during the course of a study of the Tesla luminescence spectra of benzene and some of its simple derivatives, some very interesting facts came to light in connection with the decomposition and behavior of these substances under the action of the Tesla discharge. Aside from the recent note of Harkins[3] and Gans on the decomposition of benzene, there appears to be no reliable literature on the subject of the chemical behavior of organic vapors in the electrical discharge; hence it has been thought worth while to record our experiences. It should perhaps be mentioned here that in our preliminary work several methods of excitation were tried. The results with the electrodeless discharge, later discarded because it failed to produce the desired spectra, have already been published[4] and are in agreement with the findings of Harkins and Gans.

The method finally selected was the Tesla discharge and is described in our previous paper.[5] However, it soon became evident that even with this discharge chemical changes were occurring in the vapors. This was indicated primarily by the formation on the discharge tube of shellac-like coatings similar to those formed in the electrodeless discharge, although no trace of the hydrogen lines, Swan bands, or ionized carbon lines appeared in the spectra obtained by this method. Moreover, further investigation

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[1] From a dissertation presented by J. B. Austin to the Graduate School of Yale University, June, 1928, in candidacy for the degree of Doctor of Philosophy.

[2] Commonwealth Fellow 1926–1928.

[3] Harkins and Gans, THIS JOURNAL, 52, 2578 (1930).

[4] Austin, *ibid.*, 52, 3026 (1930).

[5] Austin and Black, Phys. *Rev.*, 35, 452 (1930).

revealed that crystalline solids were being condensed along with the unchanged vapor in the liquid-air trap. In some cases these crystallized by themselves in rings high up on the walls of the trap, in others they were found dissolved in the condensed liquid; in every case, however, the quantity obtained was very small.

For general convenience in description these products will be divided into two classes, those remaining in the discharge tube and those condensed by the liquid air.

Products Remaining in the Discharge Tube.—With every material investigated save one, cyclohexane, the walls of the discharge tube became coated with a thin film of a shellac-like substance ranging in color from a deep reddish-brown and black to buff. These coatings, which seemed to adhere to the walls when fresh, showed a tendency to crack and peel off on standing.

The conditions which appeared to produce the largest yields of these materials were slightly elevated temperatures (40–50°), comparatively high pressures (0.1 mm. to 1 mm.) and large electrode surface. Since the tube tended to heat up while in operation, no external heating appliances were employed. In order to take advantage of the other factors, a new tube was designed increasing the electrode surface (Fig. 1). This tube was essentially a glass Dewar flask with the inner space between the walls, ordinarily the vacuum space, serving as the reaction chamber. Two external electrodes were used, one formed by silvering the external surface of the inner wall and the other by wrapping lead foil around the outside wall. Unfortunately this design made it necessary to cut off the tube in order to remove the coatings on the inner wall, but with this tube greatly increased yields were obtained so that enough material for study was easily made.

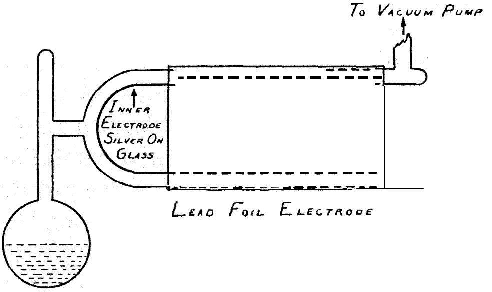

Fig. 1.—Apparatus for production of decomposition products.

An attempt to determine the properties of these materials showed them to be extraordinarily inert. They have no melting point but burn slowly with a luminous flame when heated to a sufficiently high temperature. They are insoluble in alcohol, acetone, ether, water, benzene, toluene, xylene, turpentine and ordinary acids and alkalies. Their densities as estimated by floating them in a series of alcohol–water mixtures are as follows: benzene product 0.94; toluene product 0.95; p-xylene 0.97. They appeared to have all the characteristics of highly polymerized or condensed aromatic molecules and seemed to have a number of properties in common with the products obtained by bombarding acetylene with high-speed cathode rays.[6]

Unlike the similar compounds described by Harkins and Gans they do not have the composition (CH), but appear to contain some oxygen. The C and H analyses of several of them as determined by Professor J. B. Niederl are given in Table I.

TABLE I

ANALYSES

	C, %	H, %
Benzene product	73.38	4.77
Toluene product	79.16	5.90
p-Xylene product	77.14	6.52

These are average values for five determinations, the greatest deviation from the mean being 0.30%.

It will be seen that there remains to be accounted for from 15 to 20% of the weight of these compounds. Qualitative tests for nitrogen made with a method which under ordinary conditions detects nitrogen in a sample containing 0.1%. NH_4Cl gave completely negative results; hence it has been assumed that the remaining portion is oxygen, which is the only other element likely to be present under the circumstances.

The difference between our powders and those of Harkins and Gans is, however, easily accounted for since they took great precautions to dry their vapors and in our work at least a trace of water vapor was undoubtedly present. Indeed on making a careful study of our plates we find a faint band at about λ3064, which is the position of the strongest of the so-called "water vapor" bands. Furthermore, Urey and Lavin[7] have shown that an activated oxygen carrier, probably the OH molecule, will cause the formation of acetaldehyde in ethane under the action of an electrical discharge.

It would seem probable, therefore, that under our conditions the hydrocarbon is caused to react with the free OH radicals or ions in the vapor. The simplest empirical formula corresponding to the analysis of the powder from benzene is $(C_9H_7O_2)_x$. This formula must be regarded as an approximation to a type of compound which occurs in various polymerized forms since the product obtained is probably a complex of many related substances.

It will be shown in the section on crystalline products that diphenyl is formed from benzene vapor by the discharge. There is no reason to suppose that this coupling action ceases when two rings have been joined so that we should expect to find compounds composed of a great number of benzene rings coupled in various ways. If in addition we consider the presence of the water vapor ions, it is not difficult to imagine the formation

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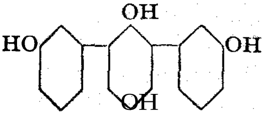
[6] McLennan, Perrin and Ireton, *Proc. Roy. Soc.* (London), 125A, 246 (1929).

[7] Urey and Lavin, THIS JOURNAL, 51, 3290 (1929).

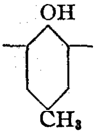
of phenolic compounds which would possess an even greater tendency to condense because of their phenolic character. This change is analogous to that observed in ethane by Urey and Lavin except that phenols are formed instead of aldehydes; this is not surprising since aldehyde formation in this case would involve the rupture of the ring.

Assuming that this coupling and phenol formation does take place, we are led to the possibility of some such compound as the following, whose formula would be $(C_9H_7O_2)_2$ (A). It should be emphasized here that we are suggesting not that this is the actual formula of the powder but that it may represent a unit in a larger complex.



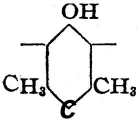
A

A study of the toluene and xylene powders lends some support to these views. The analysis of the product obtained from the former leads to the formula $(C_{21}H_{19}O_3)_x$. This may be explained by assuming a large molecule built up of (B) units, which would have the same general character as the molecule formulated for the benzene product.



B

The analysis of the xylene derivative leads to the approximate empirical formula $(C_{19}H_{19}O_3)_x$. This may be accounted for if we regard the molecular unit as (C) or C_8H_8O and if we consider the chain long enough to make the effect of the extra hydrogen atoms in the terminal rings negligible. The observed oxygen content, which is slightly above the proposed theoretical value, may be explained as arising from the presence of several phenol groups in some of the units.



C

It must be admitted that the lack of solubility in alkalies is not in accord with the phenolic character postulated, unless we assume a behavior similar to that observed in the monohydric phenols, where increasing molecular weight is accompanied by decreasing solubility. All of these remarks must await the accumulation of more data before they may be regarded as more than mere speculations; it is hoped, however, that they will provide a basis for discussion and will suggest new fields of endeavor and it is for these purposes that they are offered.

Crystalline Products

The evidence in the case of these compounds is much more conclusive than in the previous one. Since a general discussion is rather difficult until the data have been presented, the reactions of each vapor will be treated separately.

(a) **Benzene.**—After the condensate from the liquid-air trap was evaporated, the residue was examined, and was found to be a resinous matrix in which some small clear crystals were embedded. The identification of these crystals presented a number of difficulties, chief among which was the fact that so little material was available. The crystals were finally separated from the matrix by extraction with alcohol followed by partial evaporation of the resulting solution. They possessed the characteristic odor of diphenyl, their melting point was 69.5° in agreement with that of diphenyl and a mixture of these crystals with some diphenyl obtained from the Eastman Kodak Company showed an identical melting point. Moreover, the general optical properties of the unknown agreed with those of the Eastman sample. Both crystallized as flat monoclinic plates; both were strongly birefringent. Because of these conditions it was not deemed feasible to make an accurate determination of the refractive indices. However, the agreement of the general optical character added to the other evidence was regarded as sufficient proof that the unknown crystals were indeed diphenyl. It is interesting to note that these products are exactly the same as those obtained by Berthelot[8] in passing benzene vapor through a hot tube. No clue to the nature of the resinous material was obtained.

(b) Toluene.—With toluene several crystalline products were recovered. The first of these, which was found in a ring at the top of the trap, melted at 50.5°, which is in agreement with the melting point of dibenzyl. It was considered desirable to have some definite proof of the identity of this material, since it is in a sense the keystone of the series of compounds obtained with other substances. With the small amount of the unknown available, a determination of the optical properties seemed to be the most conclusive test.

In this case the refractive indices, which do not appear to have been previously recorded, were determined approximately. Since dibenzyl is soluble in the usual refractive index oils, a series of potassium iodide–mercury iodide solutions in a 50% glycerol–water mixture was used.

Dibenzyl crystallizes in monoclinic prisms which are strongly birefringent, making the exact determination of the indices rather difficult. The approximate values for the low and high indices are 1.53 and 1.74. The unknown crystals, in addition to having the crystalline form of dibenzyl, possessed approximately the correct indices. This was regarded as sufficient evidence to establish their identity.

When the liquid in the bottom of the liquid–air trap had been tapped off it was placed in an ice box for keeping. During the cooling some well-defined crystals appeared which were filtered off and dried. These were found to have the melting point (17.0") of 2,2′-dimethyldiphenyl. No determination of the indices was made but in view of the formation of diphenyl from benzene it seems likely that the identification is correct.

A small amount of sirupy liquid was obtained on evaporating the remaining condensate from the trap. This liquid did not freeze at zero and had a high boiling point (above 200°). It was impossible to identify positively such a small amount of material but it is our belief that the liquid in question was a mixture of isomers of 2,2′-dimethyldiphenyl, several of which are high-boiling liquids.

(c) *p*-**Xylene.**—In this case a few crystals melting at 81° were found. This corresponds quite well with the melting point of di-p-tolylethane (82°); this reaction is analogous to the formation of dibenzyl from toluene and receives some confirmation from the known occurrence of that reaction. Here again a bit of sirupy liquid was obtained which, while unidentified, is believed to be a mixture of high-boiling liquid isomers.

(d) Nitrobenzene.—The accumulation of tar was so great that any attempt to separate crystals seemed futile.

(e) **Chlorobenzene.**—The chlorobenzene vapor decomposed to a very considerable extent under the discharge. A strong chlorine odor was observed when the system was opened and a strong benzene spectrum was obtained. Moreover, a few crystals of diphenyl were identified in the liquid-air trap.

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[8] Berthelot, *Compt. vend.*, 62, 947 (1866).

(f) Cyclohexane.—No products were found. These reactions are summarized in Table II.

TABLE II

SUMMARY OF REACTIONS OBSERVED IN THE TESLA DISCHARGE

$2C_6H_6 = C_6H_5C_6H_5$
$2CH_3C_6H_5 = C_6H_5CH_2CH_2C_6H_5$
$2CH_3C_6H_5 = CH_3C_6H_4C_6H_4CH_3$
$2CH_3C_6H_4CH_3 = CH_3C_6H_4CH_2CH_2C_6H_4CH_3$
$4C_6H_5Cl = 2C_6H_6 + 2Cl_2 + C_6H_5C_6H_5$

Discussion

No discussion of these observations would be complete without a few speculations as to the mechanism of the reactions. Under the conditions of excitation several possibilities must be considered. Considering it axiomatic that reaction does not occur between normal unexcited molecules, we have a choice of the following: reaction between two ions, between an ion and a normal molecule, between two activated though un-ionized molecules, or between an activated and a normal molecule. Since products similar to our brown powders are produced by the electrodeless discharge and by the action of high-speed cathode rays, in which cases ionization seems to play a definite role, it would seem that we must look for reaction between ions in the present case. On the other hand, the conditions favoring increased yields, i. e., higher temperatures and pressure, lead one to suppose that collisions must also be a factor. It is probable therefore that the process by which these substances are produced requires ionization of the vapor followed by a collision of the ions with other ions or normal molecules.

The authors wish to express their appreciation to Dr. E. T. Wherry for help and advice in the matter of the optical properties of the dibenzyl, to Dr. Elizabeth Gilman Roberts for help in the qualitative tests for nitrogen, to Professor J. B. Niederl for his analyses of the brown powders and to Mr. L. E. Faulhaber for help in preparing the manuscript.

Summary

The Tesla discharge in the vapors of benzene and its simple derivatives causes chemical action with the formation of two types of compounds; first, brown shellac-like compounds containing oxygen which are left in the discharge tube and appear to be condensed molecules of a phenolic type; second, relatively simple molecules which condense in well-defined crystals. In this latter class, diphenyl is produced from benzene and dibenzyl from toluene; isomers of these compounds are also formed. The low and high refractive indices of dibenzyl have been determined and are approximately 1.53 and 1.74.

STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND]

THE DECOMPOSITION OF ETHYLENE GLYCOL IN THE PRESENCE OF CATALYSTS. I. VANADIUM PENTOXIDE AS CATALYST

BY NATHAN L. DRAKE AND THOMAS B. SMITH[1]

RECEIVED AUGUST 22, 1930 PUBLISHED NOVEMBER 5, 1930

The generation of an ethylene oxide linkage by the direct addition of oxygen to a double bond would be a useful reaction. In particular, starting from ethylene, it would be easy to prepare ethylene glycol

$$2CH_2{=}CH_2 + O_2 + 2H_2O = 2CH_2OHCH_2OH \qquad (1)$$

Francis[2] has calculated an expression for the free energy of formation of ethylene from its elements

$$AF = 12,260 + 11.6T$$

and Parks and co-workers[3] have revised their earlier calculations of the free energy of formation of liquid ethylene glycol, **giving** as their revised value

$$\Delta F_{298} = -81,800 \text{ cal.}$$

From Francis' equation, for ethylene

$$\Delta F_{298} = +15,717 \text{ cal.}$$

For liquid water[4]

$$\Delta F_{298} = -56,560 \text{ cal.}$$

Consequently, for the reaction

$$CH_2{=}CH_2(g) + {}^1/_2O_2(g) + H_2O(l) = CH_2OHCH_2OH(l)$$
$$\Delta F_{298} = -40,957 \text{ cal.}$$

There is, therefore, nothing thermodynamically unsound in an attempt to devise a method for carrying out this reaction. The use of pressure would certainly aid much in bringing about Reaction 1, and if a catalyst could be found which would render possible the production of ethylene oxide, the synthesis of glycol from ethylene, air and water should be possible.

Obviously the simplest method of testing a number of catalysts would be to examine their effect on the decomposition of ethylene glycol under various conditions. The present paper is concerned with the beginning of such a study. This method of attack permits operation at ordinary pressure in simple apparatus, and is undoubtedly the most economical of time and

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[1] From a thesis presented by T. B. Smith to the Graduate *School* of the *University* of Maryland in partial fulfilment of the requirements for the degree of Master of Science.

[2] Francis, *Ind. Eng. Chem.. 20, 279 (1928).*

[3] Parks and co-workers, THIS JOURNAL, *51,1969 (1929).*

[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical *Substances,"* McGraw-Hill Book Co., Inc., New York, 1923, p. *607.*

material. A gas analysis of the products of decomposition enables the operator to follow very easily the course of the decomposition.

Practically no work has been done on the influence of catalysts on ethylene glycol. Sabatier[5] found that glycol passed over alumina at 400° yielded chiefly acetaldehyde which polymerized partially to paraldehyde. Trillat[6] passed glycol over a platinum spiral at 90° and noted that the spiral was raised to incandescence, with decomposition of the glycol into formaldehyde, glycolic aldehyde and glyoxal.

The extended use of vanadium pentoxide as an oxidation catalyst led the authors to choose it for use in their preliminary studies. There is no reported work on the influence of vanadium pentoxide on ethylene glycol.

Preparation and Purification of Materials.—The catalyst used in these investigations was prepared from ammonium vanadate. Fused vanadium pentoxide was treated with hot concentrated (sp. gr. 1.42) nitric acid, about 150 cc. of acid for each 5 g. of vanadium pentoxide, and the solution filtered and evaporated nearly to dryness. The product separating from the solution during evaporation was filtered off, washed twice with cold distilled water to remove the greater part of the acid and dissolved in concentrated aqueous ammonia (sp. gr. 0.90). The resulting solution was again filtered and nearly saturated with ammonium nitrate which had been recrystallized from water. The solution was then allowed to stand for a period of twelve hours to allow crystallization of the ammonium metavanadate to take place. This material was dissolved in dilute aqueous ammonia and again caused to crystallize as above. The ammonium metavanadate so prepared was filtered from the solution, washed once with cold water and dried over calcium chloride in a vacuum.

The catalyst used in the decomposition studies was obtained by heating in a stream of oxygen 0.5 g, of ammonium vanadate contained in a small porcelain boat. The temperature of the furnace in which the boat was heated was raised slowly to 350°, and maintained there until no trace of ammonia could be detected issuing from the furnace. Matignon[7] has shown that vanadium pentoxide is produced from ammonium metavanadate only in this way. If the metavanadate is not heated under oxidizing conditions, a substance of the composition $5V_2O_5{\cdot}2VO_3NH_4$ results. Some preliminary experiments described below were conducted with this substance as the contact material.

The ethylene glycol used was obtained by carefully distilling commercial ethylene glycol, called Prestone, and collecting the fraction boiling at 197°.

Apparatus

The apparatus used is shown in Fig. 1: G, a pyrex tube, containing the ethylene glycol, was heated by means of the oil-bath H, whose temperature was maintained at 205" by a Bunsen burner protected from drafts by an asbestos shield. Glycol was introduced by means of a capillary into G through I, which was then closed by a piece of glass rod and a short piece of tightly fitting rubber tubing. Connecting G with the furnace F was a small capillary orifice M, electrically heated to 200°. Glycol vapor generated in G under slight pressure, passed through this orifice at a constant rate into the furnace F. The latter consisted of a 16 X 250-mm. pyrex tube fitted snugly into

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[5] Sabatier, "Catalysis in Organic Chemistry," translated by Reid, D. Van Nostrand Co., New York, 1922, pp. 234. 240.

[6] Trillat, *Bull. soc. chim.*, [3] 29, 35 (1903).

[7] Matignon, *Chem.-Ztg.*, 75, 986 (1905).

another of 20 mm., the larger tube wound with chromel ribbon for electrically heating the reaction chamber. A 35-mm. tube wrapped with asbestos sheet enclosed the reaction chamber. By means of a lamp-bank the temperature in the furnace could be regulated at will. The thermometer projected into the reaction chamber to within a few mm. of the porcelain boat containing the catalyst. E, a coil condenser, which was cooled in an ice- and salt-bath during the experiments, was provided with a condensate trap and connected to the low head scrubber D. The scrubber had a volume of 300 cc. and contained 4 *N* magnesium sulfate solution. The scrubber was connected by means of the ground-glass joint in the tube C to a gasometer B, which was provided with a tenth degree thermometer, a mercury manometer, A, an outlet tube and a connection to the analyzer. The volume of gas contained in B could be read off directly by means of graduations marked on the gasometer.

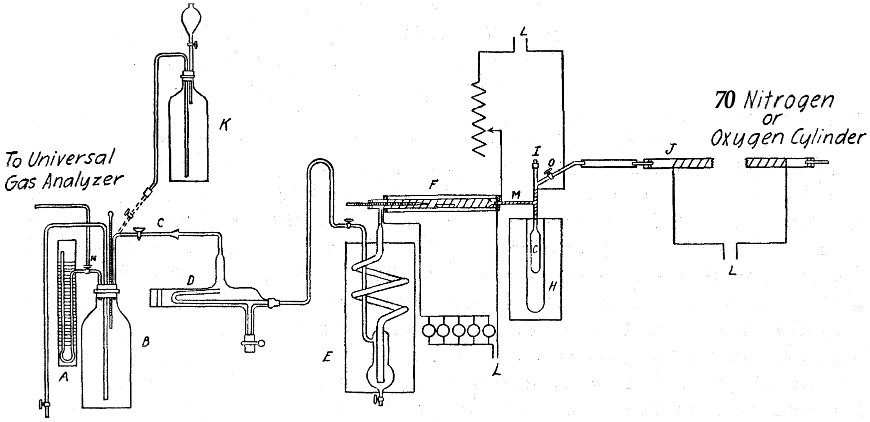

Fig. 1.—A, Manometer; B, gasometer; *C*, movable tube; D, scrubber; E, condenser; F, reaction furnace; *G*, glycol vaporizing bulb; *H*, crisco bath; **I**, bulb inlet; **J**, nitrogen purifier; K, aspirator; *L*, to 110-volt line.

The catalyst was introduced or removed through the left end of the reaction furnace, after removing the thermometer with its accompanying stopper. The products of decomposition together with the undecomposed glycol passed into the condenser, where the glycol, water and the major portion of the acetaldehyde were removed. The remainder of the acetaldehyde was removed in the scrubber. By means of the stopcock on the siphon from the gasometer, the pressure within the system from gasometer to capillary orifice could be maintained very near to atmospheric.

At the conclusion of an experiment, the tube C was disconnected at the ground joint and attached to the magnesium sulfate reservoir K. This reservoir supplied magnesium sulfate solution to replace the gas withdrawn for analysis, thus making it possible to store the gas at approximately atmospheric pressure. A Fisher Universal Gas Analyzer was used for the analytical work.

The apparatus used in fractionating the condensate consisted of a modified Claisen flask with a fractionating side arm, provided with a thermometer and connected to a small coil condenser which was cooled in an ice and salt mixture. The end of the condenser extended several centimeters below the surface of ice water contained in a 100-cc. Erlenmeyer flask.

Method.—0.5000 g. of ammonium metavanadate (equivalent to 0.3889 g. of V_2O_5) was placed in a small porcelain boat in the reaction chamber and converted into pentoxide as described above. Meanwhile, 0.1060 mole of glycol was run into the bulb G, and the reduced copper in the furnace J heated to 250°. The scrubber was filled with 4 N magnesium sulfate and the gasometer disconnected at the ground-glass joint. The system was then flushed out with nitrogen and connection again established with the gasometer. At this point gasometer and tube C were filled with the confining liquid and connected to the scrubber by means of the ground-glass joint. With the system thus prepared for collecting the reaction products, the temperature of the oil-bath H was raised to 205° and maintained there until the glycol had been vaporized completely from the container. Throughout the experiment the stopcock of the siphon tube of the gasometer was so adjusted that a 10-mm. pressure was maintained within the system. Approximately two hours was required to vaporize the glycol, whereupon a stream of nitrogen was again blown through the apparatus to sweep out the remainder of the reaction products. When approximately 1200 cc. of nitrogen had passed through the apparatus, the stopcock in C was closed and the gasometer disconnected. The catalyst was allowed to cool in a stream of nitrogen before it was removed.

Analytical Methods.—The gaseous decomposition products were analyzed in a Fisher Universal Gas Analyzer; carbon dioxide, oxygen, ethylene, carbon monoxide. hydrogen and methane were determined in the order mentioned. Successive analyses were run until the results checked to within 0.3%. Ethylene was determined by absorption in 24% fuming sulfuric acid, but a check determination was run by absorbing the gas in bromine water to confirm the results obtained by the sulfuric acid method.

In the aqueous condensate were found acetaldehyde, acetic acid and undecomposed glycol. The major portion of the acetaldehyde was slowly distilled from the mixture in the apparatus described above and collected in approximately 100 cc. of water contained in the receiver. This receiver was then replaced by another and the remaining aldehyde, the acetic acid and water were distilled into it. The Claisen flask was then weighed and the glycol distilled *in vacuo*. The distillation flask was reweighed to determine the weight of glycol distilled.

The acetaldehyde in the first portion of the distillate was determined as follows:[8] 0.5 g. of hydroxylamine hydrochloride was added to a 250-cc. portion and the resulting solution allowed to stand for thirty minutes, whereupon the hydrochloric acid liberated was titrated with $N/4$ alkali using tetrabrom phenol blue as indicator.[9]

The second fraction was analyzed as follows. The acetic acid was titrated with $N/4$ alkali, using phenolphthalein as indicator. In another portion the aldehyde was oxidized to acetic acid by alkaline hydrogen peroxide (3%), and the excess alkali was titrated with $N/4$ hydrochloric acid using phenolphthalein as indicator.[10] The difference between the amounts of acetic acid found in the two operations enables one to calculate the amount of aldehyde present in the mixture.

Any aldehyde contained in the scrubber was driven off and collected, using the same distillation apparatus as above. The amount of aldehyde in the distillate was determined by the hydroxylamine method.

Discussion of Results

By means of a carbon balance, the percentage of glycol which was decomposed on passing over the catalyst was calculated. Curve I, Fig. 2, represents graphically the results of such a calculation. The error in-

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[8] Allen's "Commercial Organic Analysis," pp. 124–140, Vol. I; original method, *Zeitschrift fur Untersuchung der Nahrungs- und Genussmittel*, *42*, 81 (1921).

[9] Harden and Drake, THIS JOURNAL, 51, 2278 (1929).

[10] Hoepner, *J. Soc. Chem. Ind.*, 38, 735 (1919).

volved in this method of computing percentage of glycol decomposed is far less than would be the case if the recovered glycol were taken as a basis for the computation. In the region between 297 and 357°, the slope of the curve is large, but below and above these points the slope decreases. Evidently, from the slope of Curve I, there is little to be gained by operating at temperatures above 400°. With the apparatus described, operation at temperatures above 400° was impossible, but the apparatus has been redesigned and we will be able in the near future to continue the curve in the region above 400°.

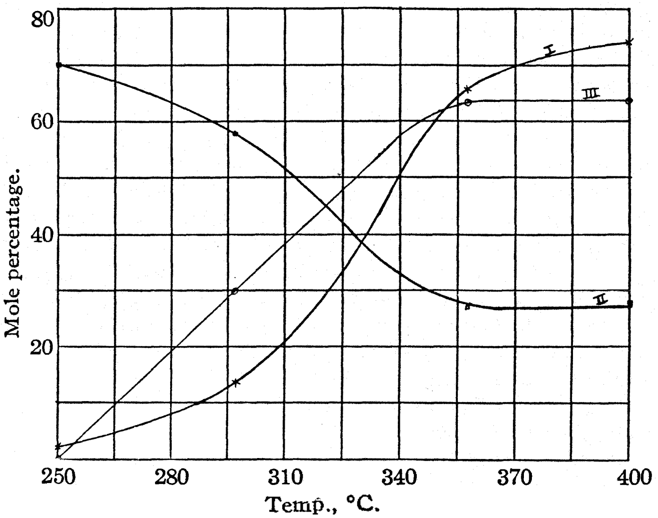


Fig. 2.—Decomposition of glycol in mole per cent. as a function of temperature.

The curves of Fig. 3 show the relation between the mole percentages of the various carbon-containing reaction products. It is very interesting and significant to note that up to a temperature of about 317°, more ethylene than any other product was produced. At 297°, for example, 7.75% of the total glycol was converted into ethylene. Referring to Fig. 2, however, we see that at this temperature 13.4% only of the glycol passing over the catalyst was decomposed. Consequently 58% of the *decomposed* glycol was converted into ethylene. Curves II and III of Fig. 2 show the relative percentages of ethylene and acetaldehyde formed, based on the glycol decomposed. It is more clearly evident from a consideration of these curves that nothing is to be gained by operation at a higher temperature. The curves for aldehyde and ethylene reach a maximum and a minimum, respectively, in the neighborhood of 357°, although the percentage of glycol decomposed increases nearly 10% between 357 and 400°.

During each experiment considerable reduction of the vanadium pentoxide took place, as shown by a color change from brick red to jet black. In the experiments from which the data for the curves of Figs. 2 and 3 were obtained, fresh catalyst was used at each temperature. That reduction of the oxide caused a considerable variation in the nature of the decomposition products was shown by using a specimen of catalyst a second time. These two experiments were conducted at a temperature of 360° in the usual fashion; the products formed are given in moles.

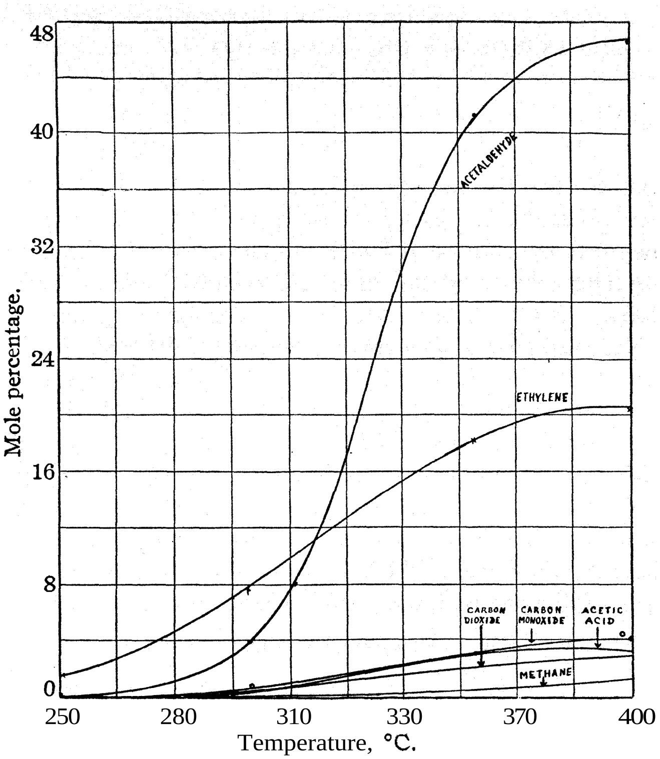


Fig. 3.—Percentage of total glycol used decomposed into acetaldehyde, ethylene, carbon monoxide, carbon dioxide, methane and acetic acid.

	I	II
CO_2	0.0045	0.0023
C_2H_4	.0196	.0145
CO	.0071	.0044
CH_3CHO	.0440	.0436
CH_3COOH	.0033	.0019

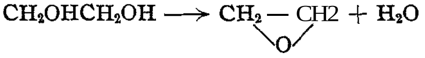
Evidently ethylene formation was more favored by the presence of fresh vanadium pentoxide than by the used catalyst, but either contact mass produced acetaldehyde in about equivalent amounts.

Two mechanisms are suggested to account for the production of aldehyde

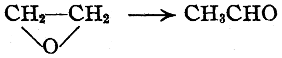
$$CH_2OHCH_2OH \longrightarrow CH_2{=}CHOH + H_2O \qquad (2)$$

$$CH_2{=}CHOH \longrightarrow CH_3CHO \qquad (3)$$

and

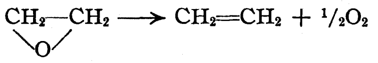


$$CH_2OHCH_2OH \longrightarrow CH_2{-}CH_2\ (-O-) + H_2O \qquad (4)$$



$$CH_2{-}CH_2\ (-O-) \longrightarrow CH_3CHO \qquad (5)$$

Ipatiev[11] has studied the behavior of oxides on heating both in the presence and absence of catalysts. Ethylene oxide passed through a glass tube was found to begin to decompose at 500°. In the presence of aluminum oxide, however, rearrangement of the oxide into acetaldehyde took place readily between 200 and 300°. The work of Nef[12] confirms in a general way that of Ipatiev. Nef observed a slow rearrangement of ethylene oxide into acetaldehyde in glass tubes at 400–420°. No evolution of gas took place in this temperature interval. The behavior of many substituted ethylene oxides on heating has been studied by Tiffeneau and Lévy[13] and Lévy and Sfiras.[14] Many of the oxides investigated undergo a rearrangement like that of ethylene oxide into acetaldehyde. This rearrangement, therefore, is common to a-oxides, and it is possible, consequently, that ethylene oxide was the intermediate from which both acetaldehyde and ethylene were formed. The following reaction would account for the ethylene



$$CH_2{-}CH_2\ (-O-) \longrightarrow CH_2{=}CH_2 + {}^1/_2O_2 \qquad (6)$$

The acetic acid is undoubtedly formed by the oxidation of acetaldehyde, and it will be seen that the contour of the acetic acid curve follows roughly that of the aldehyde curve, a condition to be expected if the acid is produced from aldehyde by oxidation.

For the production of carbon monoxide, two mechanisms are possible, and probably monoxide is formed through both. It is known that vanadium pentoxide acts as a dehydrogenation catalyst[15] and the reactions

$$CH_2OHCH_2OH \longrightarrow CHOCHO + 2H_2 \qquad (7)$$

$$CHOCHO \longrightarrow 2CO + H_2 \qquad (8)$$

readily account for the formation of carbon monoxide. It has also been

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[11] Ipatiev, *Ber.*, 36, 2016 (1903).

[12] Nef, *Ann.*, 335, 201 (1904).

[13] Tiffeneau and Lévy, *Bull. soc. chim.*, 39, 763–82 (1926).

[14] Lévy and Sfiras, *Compt. rend.*, 184, 1335 (1927).

[15] Walker, British Patent 295,356 (1929); *C. A.*, 23, 2186 (1929); Brown, U. S. Patent 1,757,830 (May 6, 1930); E. I. du Pont de Nemours and *Co.*, British Patent 323,713 (March 5, 1930).

shown[16] that at elevated temperatures acetaldehyde readily decomposes according to the equation

$$CH_3CHO = 60 + CH_4 \qquad (9)$$

This reaction accounts not only for the presence of carbon monoxide, but also predicts the simultaneous formation of methane in equivalent amount. Although the methane curve of Fig. **3** follows roughly in shape those for carbon monoxide and acetaldehyde, the methane found was always considerably less than would correspond to the carbon monoxide It is probable therefore, that Reactions 8 and 9 were each responsible for some carbon monoxide, and that the methane is produced according to 9. A small amount of hydrogen was always found in the gases. Undoubtedly most of the hydrogen formed was oxidized to water by the catalyst, but the presence of a small amount of it is evidence that Reactions 7 and 8 took place to some extent.

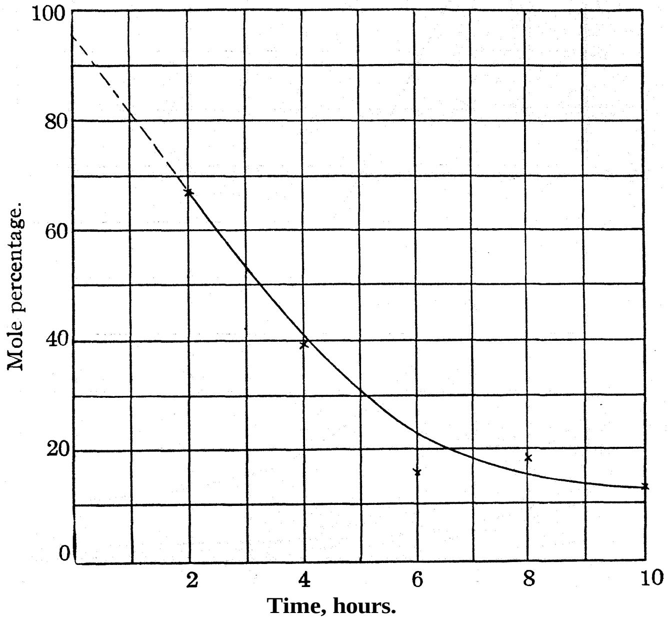

Fig. 4.—Decomposition of glycol in mole percentage plotted as a function of catalyst aging expressed in hours (temperature, 360°).

The carbon dioxide and carbon monoxide curves have the same shape, the former below the latter. Oxidation of carbon monoxide is without doubt the mechanism by which the dioxide is formed.

Figures 4 and 5 represent a series of preliminary experiments in which the compound described by Matignon[7] was used as catalyst. It will be noted that the amounts of the various products formed become rapidly less as

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[16] Peytral, *Bull. soc. chim.*, 27, 34–39 (1929); Hinshelwood and Hutchinson, *Proc. Roy. Soc.* (London), 111A, 380 (1926).

the catalyst ages. How much of this effect is due to change in physical structure of the catalyst and how much to reduction it is impossible to say. With this contact mass even the acetaldehyde concentration decreased rapidly as the catalyst aged, a situation not paralleled when vanadium pentoxide was used.

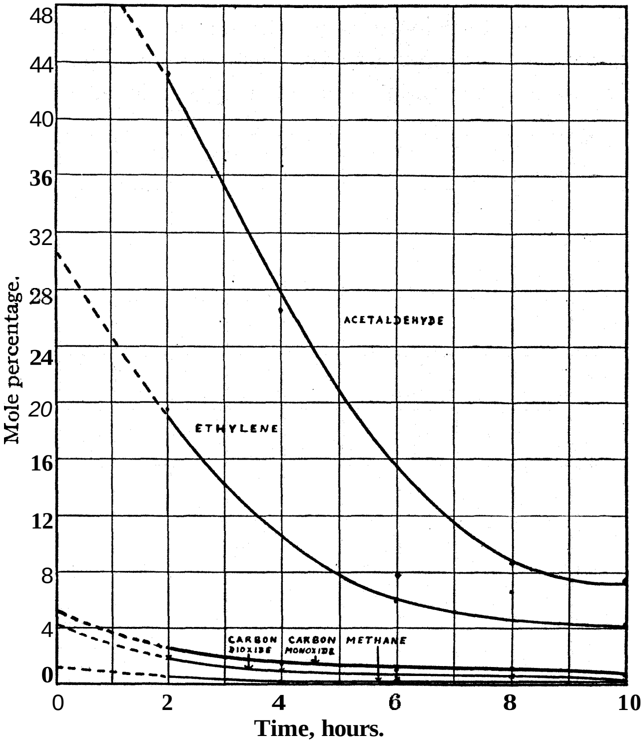

Fig. 5.—Acetaldehyde, ethylene, carbon dioxide, carbon monoxide, and methane as mole percentage of glycol used plotted as a function of the catalyst aging expressed in hours (temperature, 360°).

If the two hour points on the curves of Figs. 4 and 5 are compared with the corresponding points on Figs. 2 and 3, there is seen to be little to choose between the two catalysts.

Summary

1. The decomposition of ethylene glycol in the presence of vanadium pentoxide has been studied.
2. Acetaldehyde and ethylene are the principal products.
3. Curves showing the relative amounts of the individual products formed are given.

College Park, Maryland

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

THE QUINONOID STRUCTURE OF SOME TRIPHENYLMETHYL SALTS

BY LEIGH C. ANDERSON

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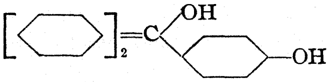
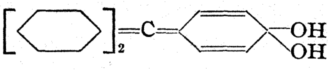
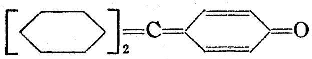
Previous papers from this Laboratory[1] have shown that a very marked change occurs in the quantitative absorption spectra when colorless @-hydroxytriarylcarbinols possessing the benzenoid structure **(I)** are converted to the tautomeric colored quinonoid carbinols (II). This type of change is especially apparent when the benzenoid carbinols are converted to the corresponding fuchsones (III) of whose quinonoid structure no question has ever been raised. It has now been found that this same marked change occurs in the quantitative absorption spectra when a colorless dimethyl sulfate solution of triphenylchloromethane is converted to triphenylmethyl sulfate or perchlorate by silver sulfate or silver perchlorate, respectively. The solution becomes yellow and at the same time the absorption of light by the solution changes in a manner similar to that which has been shown to occur when the benzenoid carbinols are converted to the quinonoid fuchsones. We have found by means of absorption spectra that triphenylchloromethane possesses the same benzenoid structure in dimethyl sulfate solutions that it possesses in ether solutions and from the similarity in the curves obtained from these two sets of reactions—benzenoid carbinols to quinonoid fuchsones and benzenoid chloride **(IV)** to sulfate or perchlorate—we are led to conclude that the salts, the sulfate and the perchlorate, exist in a quinonoid state **(V, VI)** in dimethyl sulfate solutions.



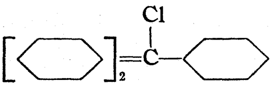
I



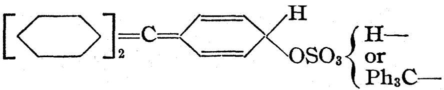
II



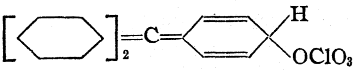
III



IV



V



VI

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[1] (a) Anderson and Gomberg, THIS JOURNAL, 50, 203 (1928); (b) Anderson, *ibid.*, 51, 1889 (1929).

This conclusion is in agreement with the chemical evidence presented by Gomberg,[2] who pointed out that the sulfates of the *p*-halogenated triphenylcarbinols are quinonoid compounds. He showed that diphenylquinomethane (fuchsone) was one of the products obtained upon hydrolysis of the sulfate of *p*-bromotriphenylcarbinol.

Former investigators have been unable to study such changes in the spectra of these salts because no one solvent had been used in which all of these compounds could be dissolved without chemical change. Gomberg[3] used dimethyl sulfate as a solvent for the preparation and purification of some of these salts, e. g., the sulfates, and he pointed out that when the solvent had been carefully purified, it yielded colorless solutions of triphenylcarbinol and triphenplchloromethane. The quantitative absorption spectra of the colorless solutions of triphenylcarbinol and triphenylchloromethane are almost identical with those curves obtained from the ether solutions of these compounds.[4] These data, together with Gomberg's work, show that pure dimethyl sulfate is without chemical effect upon these solutes. The use of dimethyl sulfate as a solvent makes it possible, therefore, for us to compare, in one solvent, the absorption spectra of the benzenoid and quinonoid salts of the triarylcarbinols.

It has been found, also, that the quantitative absorption spectra between frequencies 4200–1350 mm.^{-1} of solutions of the sulfate and perchlorate salts of triphenylcarbinol in pure sulfuric acid and pure perchloric acid, respectively, are almost identical with those obtained for each salt in its dimethyl sulfate solution; the difference between the two sets of curves lies only in the height of the quantitative curves. The similarity in the absorption bands constitutes evidence in favor of the hypothesis that these salts exist as quinonoid compounds in their solutions in these acids.

In the light of these results it appears that the questions concerning the nature of the constitution of the various salts of triarylcarbinols, which have been discussed in articles recently published by Dilthey,[5] Brand,[6] Madelung,[7] Lund[8] and others have been largely clarified and rather in favor of quinoidation.

Experimental

A drawing of the apparatus which was used to prepare solutions of the sulfate and perchlorate salts of triphenylcarbinol in dimethyl sulfate is shown in Fig. 1. Absorption

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[2] (a) Gomberg, Ber., **40**, 1853 (1907); (b) Gomberg and Blicke, THIS JOURNAL, **45**, 1770 (1923).

[3] Ref. 2a, p. 1847.

[4] Anderson, THIS JOURNAL, **50**, 208 (1928).

[5] Dilthey, *Z. angew. Chem.*, 37,313 (1924).

[6] Brand, *J. prakt. Chem.*, **109**, 17 (1925).

[7] Madelung, *ibid.*, **111**, 100 (1925).

[8] Lund, THIS JOURNAL, **49**, 1346 (1927); see also Girbes, "Dissertation," Rijks University, Groningen, **1928.**

flasks were available which had a capacity in bulb H of either 50 or 100 cc. together with absorption cells K which were fitted with parallel quartz plates through which the light was passed to be absorbed and in which the distance between the inside faces of the quartz plates was 2.4, 5.0, 7.5 or 10.0 mm. Pure silver sulfate or silver perchlorate was placed in the tube I, and a small sample of pure triphenylchloromethane, weighed directly into a micro-beaker L, was placed in the upper part of the absorption flask. In order to seal the apparatus and yet not contaminate the solvent with the lubricant, stopcocks G,G and the ground-in stopper M had very small amounts of stopcock grease on the outside edges of the ground surfaces only. Dimethyl sulfate, previously distilled under reduced pressure, was placed in flask A and the whole apparatus was evacuated by means of a water aspirator. When the manometer N indicated a pressure of 12–15 mm. of mercury within the apparatus, the silver salt in I was heated to 120–130° for fifteen to twenty minutes by means of a small electrically heated coil. After the silver salt had been dried and cooled the dimethyl sulfate was distilled through the fractionating column B and condenser C. Having collected the first fraction in F, the main portion was diverted by means of stopcock D through a 30-cm. column of freshly ignited potassium carbonate which had been placed in tube E, and from there was led into the bulb H. When H and I had been filled, stopcock D was turned to allow the last portions of the dimethyl sulfate to collect in F. The volume of the solvent contained in H and I was ascertained from calibrated graduations on the tube J immediately above the bulb H; a correction for the volume occupied by the solid silver salt in I was always applied. Following this, air was slowly admitted through the calcium chloride tube O until the pressure inside the apparatus was again equal to atmospheric. Stopcocks G,G were closed and the absorption flask, after being disconnected from the distillation set-up, was inverted to dissolve the triphenylchloromethane. The mixture was then shaken until the reaction was completed.

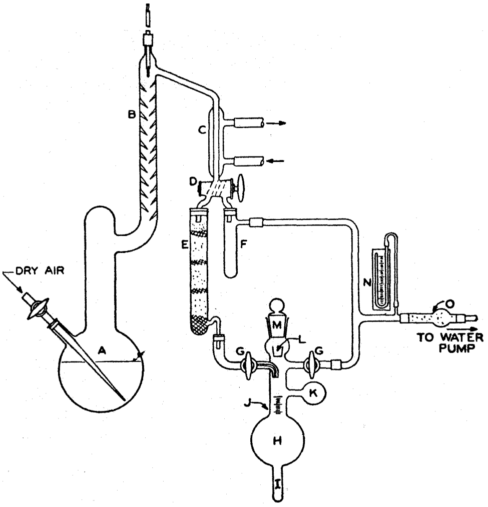


Fig. 1.

Silver perchlorate reacts rapidly with triphenylchloromethane in dimethyl sulfate and the solution acquires a brilliant yellow color. The silver chloride that is formed in the reaction is very finely divided but when the solution is allowed to stand, settles out readily. It possesses the property, however. in the dimethyl sulfate solutions, of adhering to the walls of the vessel and care was taken in the method of shaking to see that none of it was introduced into the quartz absorption cell K.

In preparing the n-sulfate of triphenylcarbinol it was necessary to keep the solution at 50–55° for a day or two before the reaction was completed and a mechanical shaking machine in an enclosed air-bath was employed. The delay in the completion of this reaction is believed to be due to the very slight solubility of silver sulfate as compared to silver perchlorate in dimethyl sulfate. The quantitative absorption spectrum of each solution was determined within a few minutes after making up the solution, and was redetermined at intervals thereafter until it was certain that the reaction was at an end.

From the fact that the absorption curves for the solutions prepared in the above manner approach a height only one-half that reached by the corresponding solutions in either sulfuric acid or dimethyl sulfate containing sulfuric acid leads to the inference that the solutes are different in the two cases. We therefore infer that in the former case, in the purified dimethyl sulfate, we were dealing with a solution of the n-sulfate.

When the potassium carbonate was omitted in the purification of the dimethyl sulfate, colored solutions were instantly obtained with either triphenylchloromethane or triphenylcarbinol. From the similarity of the absorption curve (Curve 1, Fig. 2) with that of the acid sulfate in sulfuric acid (Curve 1, Fig. 3) the inference was drawn that we were here dealing with solutions of the acid sulfate. These data corroborate the conclusion reached by Gomberg[3] that the last traces of sulfuric acid cannot be removed from dimethyl sulfate by distillation.

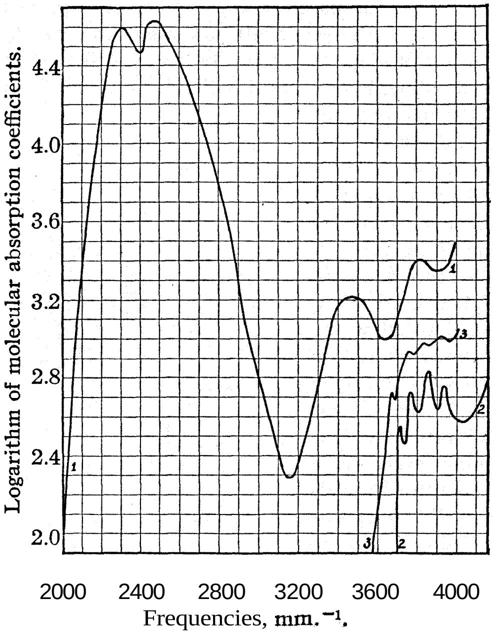


Fig. 2.—1, Triphenylmethyl acid sulfate in dimethyl sulfate; 2, triphenylcarbinol in dimethyl sulfate; 3, triphenylchloromethane in dimethyl sulfate.

The quantitative absorption spectra of triphenylcarbinol and triphenylchloromethane in dimethyl sulfate were obtained from solutions made in a manner identical with that used for the preparation of the n-sulfate and perchlorate except that no silver salt was present. Solutions of the carbinol and the chloride in dimethyl sulfate have been kept for more than a week without any development of color or of change in their absorption spectra.

Solutions for the determination of the quantitative absorption spectra of triphenylmethyl sulfate and perchlorate in sulfuric acid (95%) and perchloric acid (72%), respectively, were made by dissolving weighed amounts of either triphenylcarbinol or triphenylchloromethane in known volumes of the pure acid and taking the absorption spectra of successive dilutions.

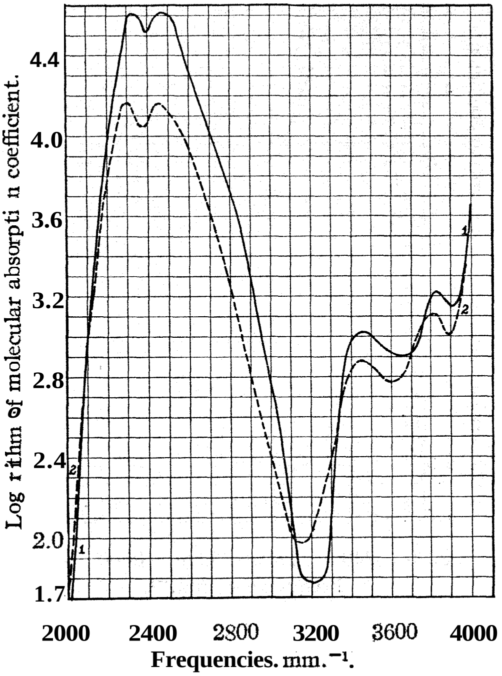


Fig. 3.—1, Triphenylmethyl acid sulfate in sulfuric acid (95%); 2, triphenylmethyl normal sulfate in dimethyl sulfate.

Attempts were made to determine the absorption spectrum of triphenylmethyl nitrate. The results thus far have not been quantitative. Silver nitrate is quite insoluble in dimethyl sulfate, and before all the triphenylchloromethane is converted to the nitrate, part of the nitrate already formed undergoes decomposition. The results that have been obtained, however, indicate that its quantitative absorption spectrum is very similar to that of the sulfate and perchlorate.

The points of maximum absorption of each—the sulfates, perchlorate and nitrate of triphenylcarbinol—were determined by a method which has been previously described[1b] and were found to be identical with each other within experimental limitations. The averages of the determinations of these points of maximum absorption lie at frequencies 2305, 2467, 3432, 3825 mm.$^{-1}$.

The writer wishes to acknowledge his deep indebtedness to Professor M. Gomberg for the suggestions and advice which have made this work possible.

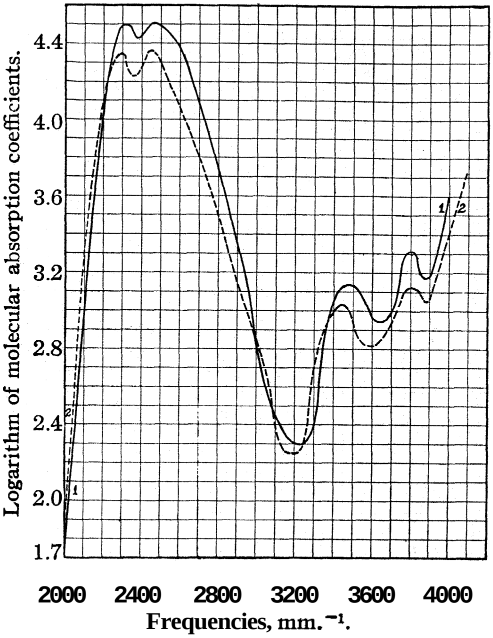


Fig. 4.—1, Triphenylmethyl perchlorate in perchloric acid (72%); 2, triphenylmethyl perchlorate in dimethyl sulfate.

Summary

1. The quantitative absorption spectra of solutions of triphenylcarbinol, triphenylchloromethane, triphenylmethyl sulfate and triphenylmethyl perchlorate in dimethyl sulfate and of solutions of the acid sulfate and of the perchlorate in sulfuric acid and perchloric acid, respectively, have been ascertained.

2. The data obtained from the absorption spectra of the above salts constitutes evidence in favor of the hypothesis that triphenylmethyl n-sulfate, acid sulfate and perchlorate exist in a quinonoid modification in their solutions in dimethyl sulfate, in sulfuric acid or perchloric acid, respectively.

Ann Arbor, Michigan

[Contribution from the Chemical Laboratory of Iowa State College]

THE FORCED REACTIOR BETWEEN ANILS AND PARA-THIOCRESOL. THE REDUCING ACTION OF THE MERCAPTO GROUPING

By Henry Gilman and J. B Dickey

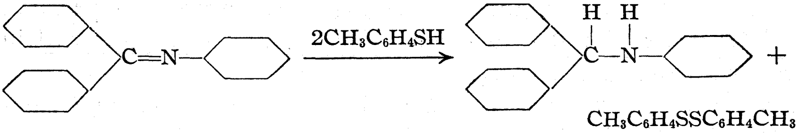
Received September 2, 1930 Published November 5, 1930

Introduction

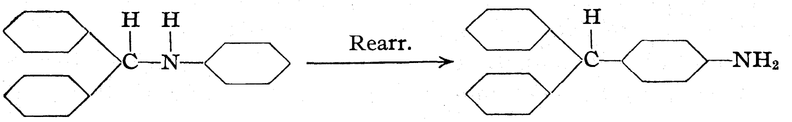
Recently, Gilman, Kirby and Kinney[1] described an unusual type of 1,4-addition to a conjugated system that is part aliphatic and part aromatic. This unique reaction which might have a significant bearing on the structure of benzene and the mechanism of substitution reactions of benzene certainly warranted confirmation with addenda other than organomagnesium halides. With this in mind, we selected *p*-thiocresol, $CH_3C_6H_4SH$, for another forced reaction study with benzophenone-anil because thiophenols lend themselves admirably as reagents for the characterization of conjugated systems.

In a preliminary experiment, in which a xylene solution of benzophenone-anil and p-thiocresol was refluxed for several hours, there was isolated a small quantity of di-*p*-tolyl disulfide, $CH_3C_6H_4SSC_6H_4CH_3$. Disulfides are formed by atmospheric oxidation of thiophenols; however, because the experiments were carried out in a trap[2] to exclude air, we concluded that the formation of di-*p*-tolyl disulfide was concomitant with reduction of the anil. This found support when the reaction products revealed *p*-thiocresol and di-p-tolyl disulfide equivalent to the initial quantity of *p*-thiocresol, and a basic compound free of sulfur, as well as some unaltered benzophenone-anil.

The basic product of reaction melted at 83–84° and it appeared altogether reasonable that it might be *p*-aminotriphenylmethane formed as a consequence of the reactions



$CH_3C_6H_4SSC_6H_4CH_3$ (II)



(III)

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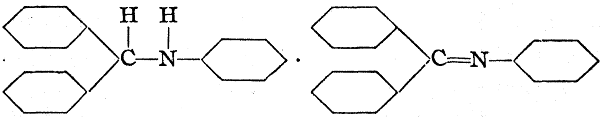
[1] Giman, Kirby and Kinney, This Journal, 51, 2252 (1929). Kohler and Nygaard, *ibid.*, 52, 4128 (1930), have just described a similar addition to the system $-CO-C_6H_5$.

[2] Gilman and Hewlett, *Rec. trav. chim.*, 48, 1124 (1929).

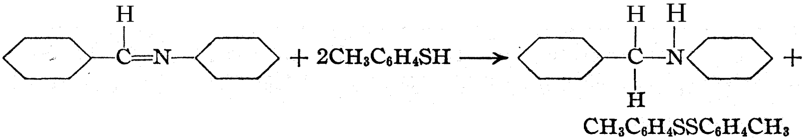
because Busch and Rinck[3] have shown that benzohydrylaniline (Reaction II) rearranges to *p*-aminotriphenylmethane when heated at an elevated temperature with aniline hydrochloride.

However, the compound was shown not to be the *p*-aminotriphenylmethane by comparison with an authentic specimen. It was subsequently established that Reaction II is correct, and that the benzohydrylaniline so formed united with a molecule of unaltered benzophenone-anil to give the complex



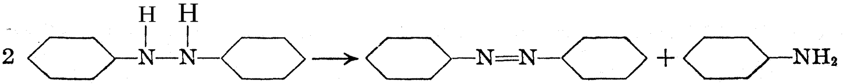
which melts at 83–84° and which is readily prepared by mixing equimolecular quantities of the two components in alcohol.[4]

The reduction of an anil is apparently a general reaction for this class of compounds inasmuch as benzalaniline was reduced rather smoothly under corresponding conditions to benzylaniline, as follows



(IV)

Likewise, azobenzene was reduced to hydrazobenzene, but under our forced conditions the hydrazobenzene underwent the known[6] thermal decomposition to azobenzene and aniline



(V)

and in the presence of an excess of the reductant (p-thiocresol) the azobenzene was progressively converted to aniline. Of course, it is possible that a part of the azobenzene may have been reduced directly to aniline, but the isolation of some hydrazobenzene (as its rearrangement product, benzidine) indicates that the reduction to aniline probably proceeded in accordance with Reaction V.

There is, then, no question concerning the reducing action of *p*-thiocresol. However, it is only a mild reducing agent, as might have been predicted from the related hydrogen sulfide and alkaline sulfhydrates. Actually, it did not reduce, under our conditions, nitrobenzene or benzophenone. It is altogether reasonable to expect that a study of other mer-

[3] Busch and Rinck, *Ber.*, 38, 1761 (1905).

[4] Alessandri, *Gazz. chim. ital.*, 51, 1, 75 (1921); C. *A.*, 15, 2860 (1921).

[5] Hofmann, *Jahresber.*, p. 425 (1863); Biehringer and Busch, *Ber.*, 36, 339 (1902); Stieglitz and Curme, *ibid.*, 46, 911 (1913); Curme, THIS JOURNAL, 35, 1143 (1913); Wieland, *Ann.*, 392, 133 (1912); *Ber.*, 48, 1098 (1915).

capto groups, alkyl as well as aryl, might reveal such compounds as useful, preferential, mild reductants.[6] However, this is beyond our immediate interests, which are concerned with the search of other addenda to support the unusual type of 1,4-addition shown by phenylmagnesium bromide.

We noted also that *p*-thiocresylmagnesium iodide, $CH_3C_6H_4SMgI$, did not react with either benzophenone-anil or benzalaniline in an ether–xylene solution. It was shown previously by Gilman and King[7] that this mercaptomagnesium halide underwent 1,4-addition with the ethylenic ketonic conjugated system in benzalacetophenone, $C_6H_5CH{=}CHCOC_6H_5$.

Experimental Part

Benzophenone-anil and *p*-Thiocresol.—In a typical experiment, 23.0 g. (0.105 mole) of benzophenone-anil[8] and 39.0 g. (0.315 mole) of p-thiocresol were dissolved in 200 cc. of xylene and refluxed for twenty-four hours in a flask connected with a trap[2] to exclude air. The cold reaction mixture was extracted with 10% sodium hydroxide to remove 13 g. or 33.3% of the thiocresol. Then the resulting mixture was concentrated under reduced pressure to remove the xylene, and the resulting oil was extracted with petroleum ether (b. p. 40–60°) and filtered. The molecular complex of benzohydrylaniline and benzophenone-anil is but slightly soluble in petroleum ether. By this treatment 15 g. or a 58% yield of the benzohydrylaniline and benzophenone-anil complex was isolated and identified by a mixed melting point determination.

The oily residue from the petroleum ether yielded 10 g. or 37% of benzohydrylaniline. This was converted to its hydrochloride, which was identified by a mixed melting point determination with an authentic specimen prepared in accordance with the directions of Busch.[9] The isolation of the benzohydrylaniline indicates that the complex with benzophenone-anil is first formed and then undergoes reduction.

Other products recovered were 22.1 g. or 56.6% of di-p-tolyl disulfide and a trace of aniline. Like products were obtained in another experiment when a small quantity of piperidine was used as a catalyst.

Benzalaniline and *p*-Thiocresol.—In one experiment 25.5 g. (0.141 mole) of benzalaniline[10] and 69.4 g. (0.564 mole) of p-thiocresol in 200 cc. of xylene were refluxed for twenty-six hours. The products obtained were 36 g. or 50.2% of p-thiocresol, 32 g. of di-p-tolyl disulfide (equivalent to 45.7% of p-thiocresol) and 19.4 g. of benzylaniline. All of the benzylaniline was not recovered, because of the difficulty of effecting a complete separation from traces of aniline and some unaltered benzalaniline. The identity of benzylaniline was confirmed by mixed melting point determinations of the hydrochloride and oxalate prepared from it, with authentic specimens of these salts.

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[6] Possibly such reduction of organic compounds by organo-mercapto groups may have been noted by others. We are unfamiliar with such studies.

[7] Gilman and King, THIS JOURNAL, 47, 1136 (1925).

[8] The benzophenone-anil was prepared in accordance with the direction of Reddelien, *Ber.*, 42, 4759 (1909). Unfortunately, the yields so obtained in several preparations were only about 20%. Single preparations were also made after the modifications of Reddelien, *Ber.*, 48, 1462 (1915), and of Knoevenagel, J. prakt. Chem., [2] 89, 37 (1913), and again with yields distinctly below those reported. Possibly the difficulty lies in varying purities of the condensing agents.

[9] Busch, *Ber.*, 37, 2691 (1904); Busch and Rinck, *Ber.*, 38, 1769 (1905).

[10] Prepared in accordance with the directions given in "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 22.

The same products were obtained in another experiment in which 0.5 cc. of piperidine was used as a catalyst.

Azobenzene and *p*-Thiocresol.—A solution of 18.2 g. (0.1 mole) of azobenzene and 37.2 g. (0.3 mole) of p-thiocresol in 200 cc. of xylene was refluxed for twenty-five hours. As in all other experiments, a trap[a] was used to exclude air. The products obtained were 9.5 g. of aniline, 0.1 g. of benzidine (from a sulfuric acid treatment of the hydrazobenzene present), 5.5 g. of p-thiocresol and 90% of the di-p-tolyl disulfide which should have formed on the basis of the reduction products isolated.

Miscellaneous.—After heating 0 075 mole of benzophenone-anil with four molecular equivalents of *p*-thiocresylmagnesium iodide in an ether–xylene solution at 103–107° for twelve hours, 96% of the anil was recovered. In addition, 0.3 g. of aniline was isolated. Another experiment under corresponding conditions yielded a 95% recovery of the anil, and traces of aniline and di-p-tolyl disulfide.

Subsequent to refluxing three equivalents of *p*-thiocresylmagnesium iodide with benzalaniline in an ether–xylene solution at 114–124° for forty hours, 96% of the *p*-thiocresol was recovered.

The recovery of p-thiocresol in an experiment in which four molecular equivalents of it were refluxed with benzophenone in xylene for twenty-six hours was 97.8%. A like recovery of p-thiocresol was had in an experiment wherein eight equivalents were heated with nitrobenzene in xylene for twenty-six hours.

Summary

In continuation of studies on the unique 1,4-addition to a conjugated system which is part aliphatic and part aromatic, benzophenone-anil and benzalaniline, respectively, were heated with *p*-thiocresol. No 1,4-addition was observed. Instead the thiocresol acted as a reducing agent, and was converted to di-p-tolyl disulfide. It also reduces azobenzene, but not nitrobenzene or benzophenone. *p*-Thiocresylmagnesium iodide did not react with the anils.

AMES, IOWA

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

THE CHLORINE DERIVATIVES OF VANILLIN AND SOME OF THEIR REACTIONS

BY L. CHAS. RAIFORD AND J. G. LICHTY

RECEIVED SEPTEMBER 8, 1930 PUBLISHED NOVEMBER 5, 1930

In previous work in this Laboratory[1] the bromine substitution products of vanillin were studied for the purpose of completing the list and to obtain derivatives with which to test further the observations of Brady and Dunn,[2] who found that "no evidence of the existence of a second isomeride has been obtained in the cases of any hydroxybenzaldoximes," but that "certain negative substituents in the benzene ring seem to favor the existence of two isomeric oximes." Since stereoisomers were not obtained from

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[1] Raiford and Hilman, THIS JOURNAL, 49, 1077, 1571 (1927); Raiford and Stoesser, 50, 2556 (1928).

[2] Brady and Dunn, J. *Chem. Soc.*, 105, 825 (1914); 107, 1859 (1915).

the bromine derivatives an adequate test of the question required the study of products containing the "more negative" substituent chlorine. The present report covers some of the data collected in that work.

The Action of Chlorine on Vanillin.—Prior to the present work Peratoner[3] chlorinated vanillin and obtained a product that was probably an impure sample of the monochloro derivative, m. p. 165°, more recently isolated by Hann,[4] which was regarded as the 5-chloro compound. Menke and Bentley[5] chlorinated vanillin in a chloroform solution and obtained a product that melted at 166°, and which was reported as a monochloro derivative, but no analytical data were recorded.[6]

To determine the positions of halogen in the three possible isomeric monochloro derivatives of vanillin, the start was made with that amino compound in which the position of the amino radical was fixed[7] as 2 by bringing it into relationship with hemipinic acid. This amino compound was diazotized and the chlorine derivative, m. p., 128°, obtained by Sandmeyer's method must be 2-chlorovanillin.

Direct chlorination of vanillin gave a monohalogenated product, m. p. 163°, in which it has been argued by Hann that chlorine occupies position 5. The third monochloro derivative, m. p. 167–168°,[8] was obtained by chlorination of 3-methoxy-4-acetoxybenzal diacetate.[9] To decide the position of chlorine in this compound, it was converted into a monobromochloro derivative, m. p. 214°, the properties of which were compared with those of an isomeric monobromochloro compound obtained from 2-amino-5-bromovanillin, the structure of which has been established by Raiford and Stoesser.[10] When the amino radical of this substance was replaced by chlorine, a monobromochlorovanillin, m. p. 187°,[11] was obtained which has chlorine in position 2, and the product must be 2-chloro-5-bromovanillin. From this it follows that the substance melting at 214° is the 5-bromo-6-chloro

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[3] Peratoner, [*Gazz. chim.* ital., *28,* 1, 235 (1898)], reported a product that melted at 158–160" and for which he recorded a chlorine content of 20.5% (calcd., 19.0).

[4] Hann, THIS JOURNAL, 47, 2000 (1925).

[5] Menke and Bentley, *ibid.,* 20, 316 (1898).

[6] In the present work it was found that although a monochloro compound, m. p. 163°, is the chief product of direct chlorination of vanillin, large excess of chlorine gives also small quantities of the isomeric 2,5- and 5,6-dichloro derivatives. This problem will be studied further to learn whether it is possible to start with pure 5-chlorovanillin and obtain these dichloro compounds in quantity.

[7] Pschorr and Sumuleanu, *Ber.,* 32, 3408 (1899).

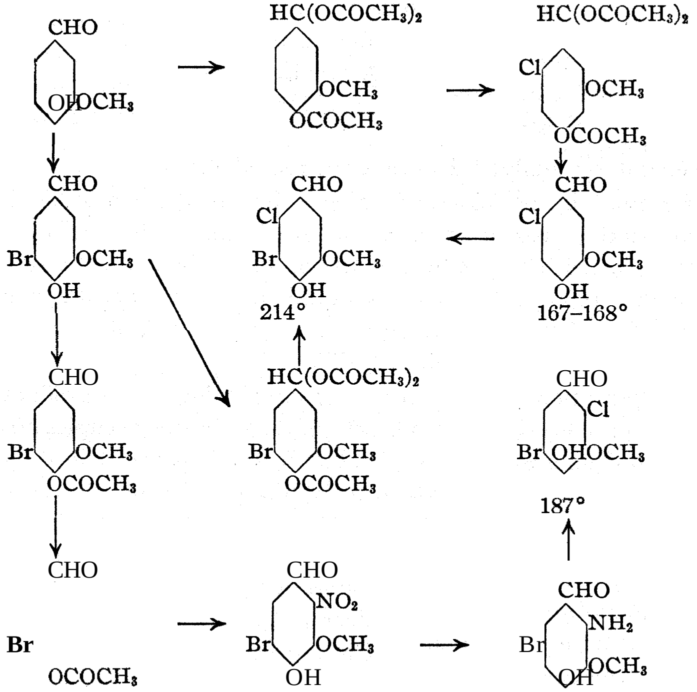
[8] A mixture of this product and that melting at 163° melted between 137 and 146°.

[9] It is of interest here to note that 6-bromovanillin was obtained in high yield [THIS JOURNAL, 49, 1079 (1927)] by bromination of acetylvanillin in the presence of sodium acetate.

[10] Raiford and Stoesser, *ibid.,* 50, 2560 (1928).

[11] ***Anal.*** Subs., 0.2041: AgHal, 0.2544. Calcd. for $C_8H_6O_3ClBr$: Hal., 43.50. Found: Hal., 43.43.

derivative, and that the chlorovanillin, m. p. 167–168°, from which it was prepared must have halogen in position 6. The monochlorovanillin, m. p. 163°, previously recorded must therefore have halogen in position 5. These relations are indicated in the diagrams.



Proof of Structure of 6-Chlorovanillin

When acetyl-5-chlorovanillin was nitrated it gave a chloronitro derivative, m. p. 137°. Reduction of this product to the corresponding amine and replacement of the amino radical by chlorine gave a dichlorovanillin that melted at 179°. Since this product was also obtained by direct chlorination of 2-chlorovanillin, the positions of the halogen atoms in this dichloro compound are shown to be 2 and 5.

It was shown above that the monochlorovanillin that melts at 167–168° is the 6-derivative. Direct chlorination of this substance gave a dichloro compound, m. p. 192°. Since this product was also obtained by chlorination of 3-methoxy-4-acetoxy-5-chlorobenzal diacetate and subsequent hydrolysis of the acetyl derivative, it follows that the final product must be 5,6-dichlorovanillin.

To obtain the third possible dichloro compound, 3-methoxy-4-acetoxy-6-chlorobenzal diacetate was nitrated, the acetyl groups removed by hydrolysis, the resulting nitro compound reduced and the amino radical replaced by chlorine. This product, melting at 139–140°, is the only remaining dichlorovanillin and must have halogen in positions 2 and 6. **Chlorination** of this compound gave a low yield[12] of 2,5,6-trichlorovanillin.

Experimental Part

The Three Monochloro Derivatives

2-Chlorovanillin.—A mixture of 14.5 g, of 2-aminovanillin,[13] 20 cc. of hydrochloric acid and 10 cc. of water was cooled below 0° and diazotized by gradually adding 6.5 g. of solid sodium nitrite. After diazotization was ,complete, a solution of 10 g. of dry cuprous chloride dissolved in 50 cc. of concentrated hydrochloric acid was added. When the copper complex was decomposed, the mixture was heated on a water-bath for a few hours, cooled and filtered. The residue was washed with dilute hydrochloric acid and then with water: yield 88%. Recrystallization from ligroin or chloroform gave pale yellow prisms, m. p. 128–129.

Anal. Subs., 0.4006: 21.65 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_8H_7O_3Cl$; Cl, 19.03. Found: Cl, 19.19.

This chlorovanillin was further characterized by the study of the derivatives indicated in Table I.

TABLE I

DERIVATIVES OF 2-CHLOROVANILLIN

No.	Compound	Solvent	Crystal form	Yield. %
1	Oxime	Dil. alcohol	Colorless needles	85
2	*p*-Bromophenylhydrazone	Dil. alcohol	Brown plates	97
3	Semicarbazone	Alcohol	Colorless plates	86
4	*Bis*-benzidine	Alcohol	Fine orange needles[a]	92

No.	Formula	M. p., °C.	Subs., g.	Cc. of 0.1 N $AgNO_3$ or wt. of AgX	Halogen, % Calcd.	Halogen, % Found
1	$C_8H_8O_3NCl$	157–158	0.4098	20.37	17.60	17.65
2	$C_{14}H_{12}O_2N_2ClBr$	144–146	.2089	0.1916	32.46	32.54
3	$C_9H_{10}O_3N_3Cl$	220–221[b]	.5510	22.80	14.58	14.69
4	$C_{28}H_{22}O_4N_2Cl_2$	224–226	.2398	0.1280	13.61	13.21

[a] When dried at 120° the color changed to red, but no evidence of solvent of crystallization was obtained.

[b] After removal of alcohol of crystallization. Anal. Subs., 0.6346: loss in wt. at 120°, 0.0836. Calcd. for one mole of C_2H_6O: 15.89. Found: 13.17.

5-Chlorovanillin.—This was obtained by a modification of Menke and Bentley's[14] method as indicated below. Excess of chlorine beyond that required for a mono-derivative was bubbled at the rate of about 10 g. of gas in fifteen minutes into a well-stirred solution of 43 g. of vanillin dissolved in 200 cc. of chloroform. Work was begun at room temperature and the temperature of the mixture was not allowed to rise above 60".

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[12] It is of interest to note here that after positions 2 and 6 have been filled by halogen, position 5 is much more readily attacked by bromine than by chlorine. Raiford and Stoesser [THIS JOURNAL, 50,2562 (1928)] obtained a 95% yield of tribromovanillin by bromination of the 2,6-derivative. In the present work a yield of only 31% of the trichloro compound was obtained, although twice the theoretical amounts of free chlorine and sulfuryl chloride, respectively, were used in separate experiments. When 2,6-dichlorovanillin was brominated a yield of 96% was obtained.

[13] Pschorr and Sumuleanu, Ber., 32,3408 (1899).

[14] Menke and Bentley, THIS JOURNAL, 20,316 (1898).

Crystals separated during the experiment and when all the chlorine had been passed in, the mixture was cooled and the solid removed by filtration. Fifty grams of vanillin was placed in the filtrate, enough chloroform added to dissolve all solid, chlorine passed in as before and the product filtered off after cooling. Repetition of the process with a second 50-g. portion of vanillin gave a total yield of 162 g. of chlorinated product or 92%. Recrystallization from acetic acid gave colorless plates; m. p. 163°. Hann found 165°. In a repetition of the experiment, treatment of the first filtrate indicated above with a much larger excess of chlorine gave a small quantity of solid which after repeated crystallizations from alcohol gave colorless needles; m. p. 174–176°. A mixture of this and pure 2,5-dichlorovanillin, m. p. 179° (see below) melted at 175–177°.

Concentration of the filtrate left after removal of the above dichloro product gave a mass of reddish colored crystals. Most of the color was removed by washing with ligroin (70–80°). Repeated crystallization of the residue from alcohol gave pale yellow needles; m. p. 188–191°. A mixture of this and pure 5,6-dichlorovanillin, m. p. 192° (see below), melted at 191–192°.

3-Methoxy-4-hydroxy-5-chlorocinnamic Acid.—A mixture of 48 g. of 5-chlorovanillin, 40 g. of freshly fused sodium acetate and 100 cc. of acetic anhydride was heated under reflux for three hours and then poured into water. The acetyl derivative separated as an oil and later solidified; yield, nearly quantitative. Extraction with boiling alcohol to remove starting material and crystallization from acetic acid gave light yellow granules; m. p. 201°.

Anal. Subs., 0.1715: AgCl, 0.2434. Calcd. for $C_{12}H_{11}O_5Cl$: Cl, 13.12. Found: Cl, 13.23.

Hydrolysis of the above product with a dilute solution of potassium hydroxide gave the free acid, which was crystallized from dilute acetone; m. p. 235–236°, with shrinking a few degrees lower.

Anal. Subs., 0.2171: AgCl, 0.1395. Calcd. for $C_{10}H_9O_4Cl$: Cl, 15.53. Found: Cl, 15.89.

5-Chlorovanillin was further characterized by study of the derivatives indicated in Table II.

TABLE II

DERIVATIVES OF 5-CHLOROVANILLIN

No.	Compound	Solvent	Crystal form	Yield, %
1	Oxime	Dil. alcohol	White needles	92
2	*p*-Bromophenylhydrazone	Dil. alcohol	Yellow plates	Nearly quant.
3	Semicarbazone	Dil. alcohol	Colorless granules	73
4	*Bis*-benzidine	Dil. pyridine	Yellow feathers	90

No.	Formula	M. p., °C.	Subs., g.	Cc. of 0.1 *N* $AgNO_3$ or wt. of AgX	Halogen, % Calcd.	Halogen, % Found
1	$C_8H_8O_3NCl$	172	0.2275	11.26	17.60	17.56
2	$C_{14}H_{12}O_2N_2ClBr$	161	.1868	0.1728	32.29	32.06
3	$C_9H_{10}O_3N_3Cl$	201	.1898	.1121	14.57[a]	14.61
4	$C_{28}H_{22}O_4N_2Cl_2$	252–254	.1310	.0725	13.61[b]	13.69

[a] Obtained after drying for eight hours at 125° to remove alcohol of crystallization. *Anal.* Subs., 0.2077: AgCl, 0.1045. Calcd. for $C_9H_{10}O_3N_3Cl \cdot C_2H_6O$: Cl, 12.28. Found: Cl, 12.45. [b] Obtained after drying for two hours at 120°. The volatile product from a second sample was conducted into ice cold water and gave the iodoform test for alcohol. *Anal.* Subs., 0.2460: loss in wt., 0.0387. Calcd. for 2 moles of C_2H_6O: 15.00. Found: 15.37. *Anal.* Subs., 0.2374: AgCl, 0.1079. Calcd. for $C_{28}H_{22}O_4N_2Cl_2 \cdot 2C_2H_6O$: Cl, 11.58. Found: Cl, 11.24.

6-Chlorovanillin.—This was obtained by chlorination of 3-methoxy-4-acetoxybenzal diacetate, which was prepared as follows. To a solution of 10 g. of vanillin dissolved in 25 cc. of acetic anhydride at about 50°, fifteen drops of concentrated sulfuric acid was added, and the red-colored mixture allowed to stand overnight. The solid was filtered off, washed with a little glacial acetic acid and the combined filtrate and washings poured into water; total yield, 97%. Crystallization from alcohol gave colorless plates; m. p. 90–91°.[15] Ten grams of this product was dissolved in 95 cc. of hot glacial acetic acid, 8 g. of finely powdered anhydrous sodium acetate added, the mixture cooled to about 40°, then about twice the calculated amount of chlorine passed in while the whole was stirred. Sodium chloride precipitated as the action proceeded. The mixture was poured into water and allowed to stand; yield, 91%. Repeated crystallization from alcohol gave colorless plates: m. p. 143–144°.

Anal. Subs., 0.2258: AgCl, 0.0989. Calcd. for $C_{14}H_{15}O_7Cl$: Cl, 10.74. Found: Cl, 10.83.

Ten grams of the chlorobenzal diacetate was boiled with a dilute solution of potassium hydroxide until all had dissolved, the mixture was cooled and 6-chlorovanillin precipitated by adding excess of hydrochloric acid; yield, 98%. Crystallization from alcohol gave colorless feathers; m. p. 167–168°.

Anal. Subs., 0.1676: AgCl, 0.1281. Calcd. for $C_8H_7O_3Cl$: Cl, 19.03. Found: Cl, 18.91.

5-Bromo-6-chlorovanillin.—This was obtained in nearly quantitative yield by slowly adding bromine to a warm glacial acetic acid solution of 6-chlorovanillin and anhydrous sodium acetate, with stirring. Crystallization from acetic acid gave colorless needles; m. p. 214".

Anal. Subs., 0.2590: AgX, 0.3233. Calcd. for $C_8H_6O_3ClBr$: X, 43.50. Found: X, 43.50.

5-Chloro-6-bromovanillin.—Excess of chlorine was bubbled with stirring into a chloroform solution of 6-bromovanillim at about 40". The product crystallized out during the reaction. By working up the mother liquor an almost quantitative yield was obtained. Recrystallization from alcohol gave nearly colorless needles; m. p. 202'.

Anal. Subs., 0.2202: AgX, 0.2741. Calcd. for $C_8H_6O_3ClBr$: X, 43.50. Found: X, 43.36.

6-Chlorovanillin was further characterized by the study of the derivatives indicated in Table III.

TABLE III

DERIVATIVES OF 6-CHLOROVANILLIN

No.	Compound	Solvent	Crystal form	Yield, %
1	Oxime	Dil. alcohol	Colorless needles	Nearly quant.
2	p-Bromophenylhydrazone	Dil. alcohol	Pale brown needles	99
3	Semicarbazone	Alcohol	Colorless needles	98
4	*Bis*-benzidine	Alcohol	Yellow, amorphous powder	92

No.	Formula	M. p., °C.	Subs., g.	Cc. of 0.1 *N* $AgNO_3$ or wt. of AgX	Halogen, % Calcd.	Halogen, % Found
1	$C_8H_8O_3NCl$	178	0.2146	0.1534	17.60	17.68
2	$C_{14}H_{12}O_2N_2ClBr$	174	.1779	.1651	32.46	32.34
3	$C_9H_{10}O_3N_3Cl$	241	.1780	.1059	14.57	14.72
4	$C_{28}H_{22}O_4N_2Cl_2$	Dec. at 263	.2403	.1311	13.61	13.50

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[15] Tiemann and Nagai, Ber., 8, 1143 (1875), found 88–89" for a product that appears to have the same composition as ours, but they reported no yield.

The Three Dichloro Derivatives

Acetyl-2-nitro-6-chlorovanillin.—Twenty grams of **3-methoxy-4-acetoxy-6-chloro**-benzal diacetate was added during a period of three minutes to 50 cc. of fuming nitric acid at 20–30° with shaking, and after standing for fifteen minutes the mixture was poured on cracked ice. The green oil that separated solidified on standing; yield, 61%. Crystallization from alcohol after boiling with norite gave nearly colorless plates that became lemon-yellow on exposure to sunlight; m. p. 81–82°.

Anal. Subs., 0.2083: AgCl, 0.1088. Calcd. for $C_{10}H_8O_6NCl$: Cl, 12.97. Found: Cl, 12.92.

2-Nitro-6-chlorovanillin.—This was obtained by hydrolysis of the acetyl derivative by alkali and by acid. The latter requires a longer time but gives a purer product with less color than was obtained with alkali. Crystallization from water gave colorless needles; m. p. 155–157°.

Anal. Subs., 0.2387: AgCl, 0.1474. Calcd. for $C_8H_6O_5NCl$: Cl, 15.33. Found: Cl, 15.27.

2-Amino-6-chlorovanillin.—Ten grams of the above nitro compound was added in small portions to a boiling mixture made from 100 g. of ferrous sulfate in 350 cc. of water and 110 cc. of concentrated ammonia water. The whole was boiled for fifteen minutes, 200 cc. of boiling water was added and the mixture was filtered while hot. The residue was repeatedly extracted with ammonia water and the collected filtrate was neutralized by dilute sulfuric acid in order to cause the amine to separate; yield, 92%. Crystallization from alcohol gave yellow needles that softened at 190° and melted at 192–193°.

Anal. Subs., 0.2750: AgCl, 0.1958. Calcd. for $C_8H_8O_3NCl$: Cl, 17.61. Found: Cl, 17.61.

2,6-Dichlorovanillin.—The amino group in the above described compound was replaced by chlorine by means of the Sandmeyer reaction; yield, 40%. Crystallization from carbon tetrachloride gave colorless needles; m. p. 139–140°.

Anal. Subs., 0.2246: AgCl, 0.2888. Calcd. for $C_8H_6O_3Cl_2$: Cl, 32.12. Found: Cl, 31.81.

This compound was further characterized by the study of the derivatives indicated in Table IV.

TABLE IV

DERIVATIVES OF 2,6-DICHLOROVANILLIN

No.	Compound	Solvent	Crystal form	Yield, %
1	Oxime	Dil. alcohol	Colorless needles	88
2	*p*-Bromophenylhydrazone	....	....	..
3	Semicarbazone	90% alcohol	Colorless needles	98
4	Bis-benzidine	Insoluble	Red, amorphous granules	Nearly quant.

No.	Formula	M. p., °C.	Subs., g.	Cc. of 0.1 *N* $AgNO_3$ or wt. of AgCl	Halogen, % Calcd.	Halogen, % Found
1	$C_8H_7O_3NCl_2$	141	0.2391	0.2910	30.08	30.12
3	$C_9H_9O_3N_3Cl_2$	213	.2134	.2199	25.53	25.54
4	$C_{28}H_{20}O_4N_2Cl_4$	232	.1880	.1788	24.06	23.52

Acetyl-5-chlorovanillin.—A mixture of 10 g. of 5-chlorovanillin, 10 cc. of glacial acetic acid and 20 cc. of acetic anhydride was refluxed for an hour and then poured into water. The oil that separated solidified after standing for one day. Many recrystallizations from ligroin gave colorless needles that melted at 67°. When distilled at 5 mm. it passed over at 167–172°, and solidified to colorless crystals; yield, nearly quantitative.

Anal. Subs., 0.2428: AgCl, 0.1525. Calcd. for $C_{10}H_9O_4Cl$: Cl, 15.53. Found: Cl, 15.53.

Acetyl-2-nitro-5-chlorovanillin.—Five grams of the above described product was slowly added to 20 g. of fuming nitric acid with shaking, while the mixture was kept at 20" or below, and then poured on cracked ice; yield, nearly quantitative. Repeated crystallization from alcohol gave colorless needles that contained one molecular proportion of alcohol of crystallization; m. p., 95–96°.

And. Subs., 0.2118: AgCl, 0.0957. Calcd. for $C_{10}H_8O_6NCl{\cdot}C_2H_6O$:[16] Cl, 11.11. Found: Cl, 11.18,

2-Nitro-5-chlorovanillin.—The acetyl derivative was warmed with potassium hydroxide solution until a clear liquid was obtained, and then an excess of dilute sulfuric add was added. Crystallization of the yellow precipitate from 20% alcohol gave pale yellow needles; m. p. 137°.

Anal. Subs., 0.1950: AgCl, 0.1214. Calcd. for $C_8H_6O_5NCl$: Cl, 15.33. Found: Cl, 15.40.

2-Amino-5-chlorovanillin.—Ten grams of the above nitro compound was reduced by means of ferrous hydroxide as explained above, with the exception that the filtrate was not neutralized by acid. The amine crystallized from the filtrate on cooling, and concentration of the mother liquor gave a second crop; yield, 87%. Recrystallization from water gave light brown needles; m. p. 136–137".

Anal. Subs., 0.1935: AgCl, 0.1374. Calcd. for $C_8H_8O_3NCl$: Cl, 17.59. Found: Cl, 17.56.

2,5-Dichlorovanillin.—A portion of the amine was dissolved in dilute hydrochloric acid cooled to about 0" and diazotized by slowly adding sodium nitrite. Cuprous chloride dissolved in concentrated hydrochloric acid was now added to the dark red mixture, which was next heated on a water-bath for two hours. The solid was filtered off, washed with dilute acid, dried and extracted with hot acetone. The extract was boiled with norite, filtered and the filtrate mixed with water; yield. 83%. Recrystallization from acetone gave colorless needles; m. p. 179°.

Anal. Subs., 0.2691: AgCl, 0.3494. Calcd. for $C_8H_6O_3Cl_2$: Cl, 32.12. Found: Cl, 32.12.

When an excess of chlorine was bubbled into 100 cc. of chloroform solution containing 1 g. of 2-chlorovanillin and the solvent distilled off, there was left nearly a quantitative yield of dichloro derivative mixed with some red resinous material. Crystallization from acetone gave colorless needles that melted at 179°, and were found by a mixed melting point to be identical with the 2,5-derivative described above.

This dichlorovanillin was further characterized by a study of the derivatives indicated in Table V.

3-Methoxy-4-acetoxy-5-chlorobenzal Diacetate.—This product was obtained in 97% yield by refluxing for one and one-half hours a solution containing 15 g. of 5-chlorovanillin in 45 cc. of acetic anhydride with one drop of concentrated sulfuric acid and pouring into water. By boiling the alcoholic solution of the deep red solid with norite, filtering and crystallizing, it was obtained in light brown plates; m. p. 115–116°.

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[16] A sample dried for six hours under reduced pressure at 80° lost alcohol and left a residue that melted at 112". *Anal.* Subs., 0.2953: AgCl, 0.1555. Calcd. for $C_{10}H_8O_6NCl$: Cl, 12.98. Found: Cl, 13.03.

TABLE V

DERIVATIVES OF 2,5-DICHLOROVANILLIN

No.	Compound	Solvent	Crystal form	Yield, %
1	Oxime	Dil. alcohol	Colorless needles	Nearly quant.
2	*p*-Bromophenylhydrazone	Dil. alcohol	Nearly colorless needles	Nearly quant.
3	Semicarbazone	Dil. pyridine	Colorless needles	89
4	*Bis*-benzidine	Pyridine	Yellow plates	98

No.	Formula	M. p., °C.	Subs., g.	Cc. of 0.1 *N* AgNO$_3$ or wt. of AgX	Halogen, % Calcd.	Halogen, % Found
1	$C_8H_7O_2NCl_2$	158	0.2196	0.2671	30.05	30.08
2	$C_{14}H_{11}O_2N_2Cl_2Br$	158	.1745	.2104	38.68	38.33
3	$C_9H_9O_3N_3Cl_2$[a]	228	.1825	.1890	25.51	25.62
4	$C_{28}H_{20}O_4N_2Cl_4$	254–255	.1379	.1325	24.04	23.77

[a] This compound crystallizes with one molecular proportion of water, which was removed by drying to constant weight at 120°. The hydrated form gave the following data. *Anal.* Subs., 0.1565: AgCl, 0.1505. Calcd. for $C_9H_9O_3N_3Cl_2 \cdot H_2O$: Cl, 23.94. Found: Cl, 23.79.

Precipitation from alcoholic solution by addition of water gave a colorless solid of the same melting point.

Anal. Subs., 0.2123: AgCl, 0.0926. Calcd. for $C_{14}H_{15}O_7Cl$: Cl, 10.74. Found: Cl, 10.79.

3-Methoxy-4-acetoxy-5,6-dichlorobenzal Diacetate.—Excess of chlorine was bubbled into a well-stirred solution of 5 g. of the above described diacetate and 4 g. of anhydrous sodium acetate in 75 cc. of glacial acetic acid, the mixture poured into water and allowed to stand for several hours; yield, 85%. Crystallization from alcohol gave colorless needles; m. p. 117–118°. A mixture of this and the starting material melted at 100–105°.

Anal. Subs., 0.1968: AgCl, 0.1544. Calcd. for $C_{14}H_{14}O_7Cl_2$: Cl, 19.44. Found: Cl, 19.41.

TABLE VI

DERIVATIVES OF 5,6-DICHLOROVANILLIN

No.	Compound	Solvent	Crystal form	Yield, %
1	Oxime	Alcohol	Colorless plates	99
2	*p*-Bromophenylhydrazone	Acetic acid	Yellow needles	66
3	Semicarbazone[a]	Alcohol	Colorless needles	93
4	*Bis*-benzidine	Alcohol	Fine yellow needles	Nearly quant.

[a] *Anal.* Subs., 0.1789: AgCl, 0.1609. Calcd. for $C_9H_9O_3N_3Cl_2 \cdot C_2H_6O$: Cl, 21.91. Found: Cl, 22.25. *Anal.* Subs., 0.1839: loss in wt., 0.0212. Calcd. for 1 mole of C_2H_6O: 14.19. Found: 11.53.

No.	Formula	M. p., °C.	Subs., g.	Cc. of 0.1 N AgNO$_3$ or wt. of AgX	Halogen, % Calcd.	Halogen, % Found
1	$C_8H_7O_3NCl_2$	203 with dec.	0.2390	0.2904	30.08	30.06
2	$C_{14}H_{11}O_2N_2Cl_2Br$	163–164[a]	.2307	.2707	37.87	37.30
3	$C_9H_9O_3N_3Cl_2$	237[b]	.1627	.1683	25.53	25.64
4	$C_{23}H_{20}O_4N_2Cl_4$	Dec. at 289°	.2562	.2447	24.04	23.63

[a] On further crystallization the melting point decreased to 147–157°. Anal. Subs., 0.2499: AgX, 0.2707. Calcd. for $C_{14}H_{11}O_2N_2Cl_2Br \cdot C_2H_4O_2$: X, 33.55. Found: X, 34.44. [b] Dried to constant weight at 120°.

The compound just described was hydrolyzed by boiling with 10 *N* potassium hydroxide solution into 5,6-dichlorovanillin, which was obtained as the sparingly soluble potassium salt. This was decomposed by dilute sulfuric acid and the product crystallized from alcohol; m. p. 192°.

Anal. Subs., 0.1688: AgCl, 0.2196. Calcd for $C_8H_6O_3Cl_2$: Cl, 32.12. Found: Cl, 32.19.

Trichlorovanillin and Derivatives

2,5,6-Trichlorovanillin.—To a saturated chloroform solution of 3 g. of 2,6-dichlorovanillin, 4 cc. of sulfuryl chloride was added, the mixture protected from moisture of the air and allowed to stand for twenty-four hours. The solvent was allowed to evaporate at room temperature and the reddish residue was fractionally crystallized from dilute alcohol. Nearly colorless needles, m. p. 154°, were obtained; yield, 31%.[17]

Anal. Subs., 0.1612: AgCl, 0.2704. Calcd. for $C_8H_5O_3Cl_3$: Cl, 41.68. Found: Cl, 41.49.

2,6-Dichloro-5-bromovanillin.—The required amount of bromine was added to a warm acetic acid solution of 2,6-dichlorovanillin and sodium acetate, the mixture allowed to stand for fifteen minutes and then poured into water; yield, 96%. The product was dissolved in hot acetic acid, hot water was added until precipitation began, the mixture was heated until clear and then allowed to cool. Small colorless needles were formed; m. p. 167°.

Anal. Subs., 0.1715: AgX, 0.2713. Calcd. for $C_8H_5O_3Cl_2Br$: X, 50.33. Found: X, 50.29.

Trichlorovanillin was further characterized by the preparation of the following derivatives. The oxime was obtained in 94% yield by the usual method. Crystallization from alcohol gave colorless needles; m. p. 173°.

Anal. Subs., 0.1665: AgCl, 0.2654. Calcd. for $C_8H_6O_3NCl_3$: Cl, 39.37. Found: Cl, 39.43.

The semicarbazone was obtained in 92% yield. Treatment of its hot alcoholic solution with hot water until precipitation began and allowing to cool gave colorless needles; m. p. 219°.

Anal. Subs., 0.1480: AgCl, 0.2001. Calcd. for $C_9H_8O_3N_3Cl_3$: Cl, 34.07. Found: Cl, 33.45.

Summary and Conclusions

1. The list of possible chlorine substitution products of vanillin has been completed. Each has been characterized by the study of several derivatives.
2. In the reactions which involved the aldehyde radical, the presence of ortho substituents caused no noticeable hindrance.
3. When chlorine is allowed to react on a vanillin derivative it does not always enter the same position as does bromine under the same conditions, which shows that the position taken is, in part, dependent on the character of the entering substituent.
4. In no case was there obtained more than one of the stereoisomeric

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[17] Unchanged starting material was recovered from the mother liquors.

oximes demanded by theory. The one obtained, probably the *anti* form, could not be transmuted by hydrogen chloride.

5. Further work is in progress in this Laboratory.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

PYROLYSIS OF ALLYLANILINES

BY F. L. CARNAHAN[1] AND CHARLES D. HURD

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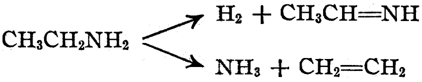
Allylaniline sufficiently resembles ethylamine and allyl phenyl ether in structure so that its pyrolysis may be considered to have points of similarity with theirs, both of which have been previously investigated. Primary effects of dehydrogenation and of deammonation have been shown to be the case[2] with ethylamine

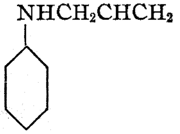


$$\begin{tikzcd} & H_2 + CH_3CH{=}NH \\ CH_3CH_2NH_2 \arrow[ur] \arrow[dr] & \\ & NH_3 + CH_2{=}CH_2 \end{tikzcd}$$

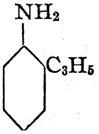
Most of the secondary reactions were traceable to the acetaldimide, chief of which was the further dehydrogenation into methyl cyanide or the demethanation into hydrogen cyanide.

For allylaniline to undergo the deammonation reaction the products would be aniline and allene. No allene was found in spite of careful search for it. The dehydrogenation reaction would give rise to acrolein-anil or its products of polymerization: $CH_2{=}CHCH_2NHC_6H_5 \longrightarrow H_2 + CH_2{=}CHCH{=}NC_6H_5$. Diallylaniline, $C_6H_5N(CH_2CH{=}CH_2)_2$, would give rise to acrolein-anil polymers by loss of propylene. Both of these reactions seem to occur. However, the fact that considerable aniline is formed during the pyrolysis of both mono- and di-allylaniline shows that this is not the exclusive feature.

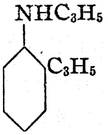
Allyl phenyl ether, on refluxing, has been shown to rearrange[3] into *o*-allylphenol. Similarly, N-allylaniline might be expected to change into o-allylaniline, and N,N-diallylaniline into either o-allylphenylallylamine or 2,6-diallylaniline. Inasmuch as pyrolysis of allyl phenyl ether gave rise



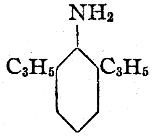
N-Allylaniline



o-Allylaniline



o-Allylphenyl-allylamine



2,6-Diallylaniline

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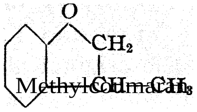
[1] Du Pont Fellow, 1929–1930.

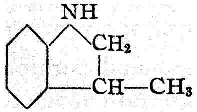
[2] Hurd and Carnahan, THIS JOURNAL, 52, 4151 (1930).

[3] For a discussion of this subject, see Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., Inc., New York, 1929, p. 215.

to a small yield of methylcoumaran in addition to the *o*-allylphenol, so it might be anticipated that N-allylaniline should give rise to methylindoline,



Methylcoumaran



Methylindoline

Preliminary study[4] of allyl- and diallylaniline indicated **a** pyrolysis on refluxing. The former changed partially into a primary amine, but it was not ascertained whether or not this was *o*-allylaniline. Similarly, the tertiary amine, diallylaniline, gave rise to both primary and secondary amines. Dains[5] found that the products obtained on heating allylaniline in a sealed tube at 250° for eight hours were unchanged amine, aniline, unsaturated gaseous hydrocarbons and a large amount of non-basic tarry material.

In this investigation it was established that the only primary amine formed from either allyl- or diallylaniline was aniline itself. It was further established that the secondary amine from diallylaniline was monoallylaniline and not o-allylphenylallylamine. Although diallylaniline is the ammono analog of allyl phenyl ether, and although both substances possess a similar instability, it is apparent that the final products of the reaction are not strictly comparable in the two cases; but this should not be interpreted to mean that no analogy exists. Diallyl-*p*-phenetidine, C_2H_5O-C_6H_4-$N(C_3H_5)_2$, was studied and its pyrolysis was found to be very similar to that of diallylaniline. Before discussing a mechanism of the pyrolysis, the general results will be outlined briefly.

General Discussion of Results

Propylene, in a fair state of purity, was liberated when either diallylaniline or diallyl-*p*-phenetidine was refluxed. It came more rapidly from the latter because of the higher reflux temperature (275°). Some diallylaniline was recoverable after two days of refluxing. Some allylaniline and larger amounts of aniline were isoluble. With diallylphenetidine, none was recoverable even when the reflux period had been shortened to two hours, nor was monoallylphenetidine found, but a large quantity of phenetidine was produced. In both cases over half of the original tertiary amine was changed into a non-volatile (at 23 mm. and 300°), brittle, black resin. The resin from diallylaniline possessed an average molecular weight of 783.

With monoallylaniline, the reflux temperature was too low for rapid pyrolysis. Accordingly, it was heated at 275° in a sealed tube. Aniline, gas and non-volatile tar were formed. When allylaniline vapor was

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[4] H. Greengard and C. D. Hurd, unpublished results.

[5] Dains, Brewster, Blair and Thompson, THIS JOURNAL, 44, *2638* **(1922).**

passed through a pyrex tube at 600° at such a rate that a hot contact time of two and one-half minutes was maintained, a similar but more deep-seated pyrolysis occurred. A 14-g. sample gave nearly 5 g. of aniline, 2.3 g. of unidentified liquids, 0.5 g. of benzene, 2.3 g. of tar and 1.3 liters of gas (hydrogen, olefins and paraffins). None of the original allylaniline was recovered. A similar change occurred at 700° when the contact time was shortened to thirty-nine seconds. From a 50-g. sample the following substances were identified: 5.7 liters of gas, 4.5 g. of benzene, 19 g. of aniline, 1–2 g. of quinoline, 7.0 g. of other liquids and 8 g. of residue. The benzene which was produced in these high temperature experiments undoubtedly was formed by the splitting action of hydrogen on aniline (or aniline derivatives), an effect which has been previously established.[6]

The moles of the more important reaction products have been summarized in Table I.

TABLE I

MOLES OF REACTION PRODUCTS FORMED

Amine used	Moles taken	Moles converted into tar	Substances formed, moles Propylene	Aniline or phenetidine	Allylaniline	Benzene
Diallylaniline (reflux)	0.146	0.104	0 038	0.035	0.011	...
Diallyl-p-phenetidine (reflux)	.138	.080	.062	.091	...	...
Allylaniline (reflux)	.044	.029	...	.011	...	...
600°	.105	.017	...	.054	...	0.007
700"	.376	.060	...	.204	...	.06

A preliminary study of **acyl-allylanilines**, C_6H_5N (allyl) (acyl), wherein the acyl group was acetyl and *p*-toluenesulfonyl.—Allylacetanilide, b. p. 149° at 24 mm., was prepared in 71% yield by the reaction of allylaniline and acetyl chloride in absolute ether. About two-fifths of it was recovered after four and one-half hours' heating at 300°. The remaining three-fifths was changed into higher-boiling material. Only a little gas was liberated. With allyl-p-toluenesulfonanilide, the decomposition at 300° was complex. Hydrogen sulfide was evolved and resin formation took place. Only traces of primary amine derivatives were formed in either case.

Mechanism of Pyrolysis of Allylanilines.—Resin formation may be accounted for through the intermediate acrolein-anil by the equations

$$\text{Ar—NHC}_3\text{H}_5 \longrightarrow \text{H}_2 + \text{Ar—N=CH—CH=CH}_2$$
$$\text{Ar—N(C}_3\text{H}_5)_2 \longrightarrow \text{C}_3\text{H}_6 + \text{Ar—N=CH—CH=CH}_2$$

No doubt these reactions do occur, and the presence of hydrogen from allylaniline provides an explanation for the presence of aniline: $ArNHC_3H_5 + 2H \longrightarrow ArNH_2 + C_3H_6$. This is a reasonable equation for the 600 and 700° experiments, but a rather doubtful one for the others. However, aniline was formed generously in all cases. Furthermore, just as much aniline (and phenetidine) was formed when the diallyl derivatives

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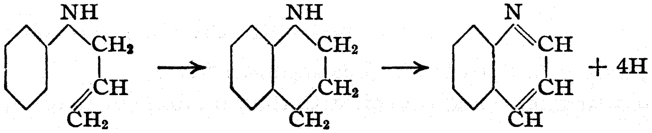
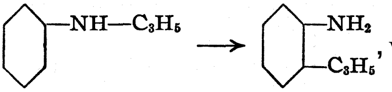
[6] Fischer and Schrader, *Brennstoff-Chem.*, 1, 4, 22 (1920).

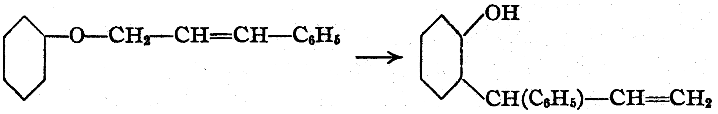
were heated as when monoallylaniline was taken, but the equation permits of no hydrogen formation with the diallyl derivatives. Aniline (or phenetidine) was not formed by direct cleavage, since allene was not formed.

Although allyl phenyl ether is known to pyrolyze into o-allylphenol, the ammono analogs in this case appear not to behave in a parallel manner. Thus, N-allylaniline does not pyrolyze into o-allylaniline. However, a carbon-to-carbon union at the ortho position was demonstrated in the 700° experiments with the isolation of quinoline. The following plan suggests itself to explain its presence

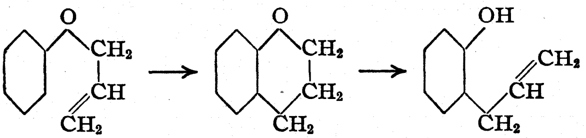


Such a series of reactions may seem to have little in common with the rearrangement  , which was discussed above.

However, it is important to note that it is the third carbon from the N which becomes attached to the ortho nuclear carbon. As Claisen[7] has demonstrated, such is also the case in allyl aryl ethers, as witnessed by the equation



The mechanism for such a rearrangement is speculative, but it is conceivable that it proceeds through a 6-membered oxygen ring. To illustrate with allyl phenyl ether



Quinoline, from allylaniline, may be explained in another fashion by assuming rearrangement to o-allylaniline, isomerization to 2-methylindoline, dehydrogenation to 2-methylindole, and rearrangement[8] to quinoline. Unidentified bases which may have contained tetrahydroquinoline, 2-methylindoline or 2-methylindole were produced in all experiments.

No single reaction seems adequate to explain the complex picture which this subject presents. It seems, however, that there are at least two major

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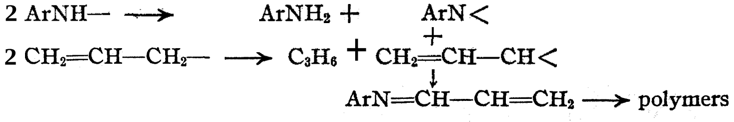
[7] Claisen and Tietze, *Ber.*, 58, 275 (1925).

[8] The rearrangement of 2-methylindole into quinoline by passing it through a hot tube has been reported by Pictet, *Ber.*, 38, 1949 (1905).

effects. One is the reaction of ring closure, giving bicyclic products. Fundamentally this seems related to the pyrolysis of allyl aryl ethers. The other effect is one which is caused by the loose type of union between the allyl radical and the nitrogen. It is convenient to picture this reaction as

$$\text{Ar—NH—C}_3\text{H}_5 \longrightarrow \text{ArNH—} + \text{—CH}_2\text{—CH=CH}_2$$

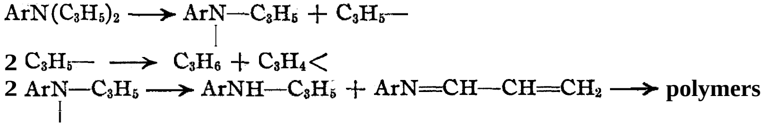
after which the radicals should disproportionate



$$\begin{array}{lll} 2\,\text{ArNH—} \longrightarrow & \text{ArNH}_2 + & \text{ArN<} \\ & & + \\ 2\,\text{CH}_2\text{=CH—CH}_2\text{—} \longrightarrow & \text{C}_3\text{H}_6 + & \text{CH}_2\text{=CH—CH<} \\ & & \downarrow \\ & & \text{ArN=CH—CH=CH}_2 \longrightarrow \text{polymers} \end{array}$$

Propylene, aniline and resins are thus accounted for.

A similar situation would prevail with diallylaniline or diallyl-*p*-phenetidine



$$\begin{array}{l} \text{ArN(C}_3\text{H}_5)_2 \longrightarrow \underset{|}{\text{ArN}}\text{—C}_3\text{H}_5 + \text{C}_3\text{H}_5\text{—} \\ 2\,\text{C}_3\text{H}_5\text{—} \longrightarrow \text{C}_3\text{H}_6 + \text{C}_3\text{H}_4\text{<} \\ 2\,\underset{|}{\text{ArN}}\text{—C}_3\text{H}_5 \longrightarrow \text{ArNH—C}_3\text{H}_5 + \text{ArN=CH—CH=CH}_2 \longrightarrow \text{polymers} \end{array}$$

This mechanism calls for allylaniline as an intermediate product. Some was isolated from diallylaniline, but for the most part it suffers further pyrolysis as outlined above.

The polymeric material with an average molecular weight of 783 may represent $(\text{C}_6\text{H}_5\text{N=CHCH=CH}_2)_6$, which has a molecular weight of 786. To ascertain whether the polymerization reaction was justified, acrolein and aniline were made to interact at 10°. A yellow resinous solid was formed which melted at about 76°. On heating, it changed into higher-melting resins which resembled those derived from the allylanilines. The reactivity of such anils is also evidenced in ethylidene-aniline, $\text{C}_6\text{H}_5\text{N=CHCH}_3$, which is known[9] to change into 1,3-dianilino-1-butene at 10°. The resins from the pyrolysis of diallylaniline were similar but not identical in appearance with the material from acrolein and aniline. This would be expected, however, in view of the presence of such radicals as C_3H_4, etc., with which the acrolein-anil could also unite.

Experimental Part

General Method of Investigation of Pyrolytic Products.—The mixtures obtained from the action of heat on allylanilines were subjected to fractional distillation first at atmospheric pressure and then under diminished pressure until only very high-boiling resinous material remained in the flask. The intermediate cuts in which were found the anilines were treated with *p*-toluenesulfonyl chloride in the presence of an excess of 10% potassium hydroxide solution. After standing for several hours the mix-

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[9] Von Miller, Plochl and Eckstein, *Ber.*, 25, 2030 (1892).

the nearly colorless liquid was 239–240° at 746 mm,, 148° at 45 mm. and 123" at 18 mm. Its index of refraction, n_D^{23}, was 1.5556. It gave tests for only a trace of secondary amine and contained no primary amine.

Pyrolysis **by Refluxing.**—A 30-g. sample of diallylaniline was placed in a 100-cc. long-necked round-bottomed pyrex flask to which was sealed a piece of tubing 1 cm. in diameter and 60 cm. long to serve as an air condenser. A thermometer rested on the bottom of the flask and extended into the condenser. The flask was heated in a fused salt bath which was maintained at about 255". With a reflux maintained at about 25 cm. above the liquid level, the temperature fell from the initial value of 240° to 228.5' in forty-eight hours.

About one liter of gas was evolved. Analysis showed the presence of 0.5% of carbon dioxide, 86.1 propylene, 0.5 ethylene, 0.7 oxygen, 3.4 hydrogen, 1.0 carbon monoxide, 3.4 paraffins (n in C_nH_{2n+2} was 1.7) and 4.4% of nitrogen. The identification of the main portion of the gas as propylene rather than allene was made in another run (40 g.) in which the gas evolved was passed into a solution of 18 g. of dry bromine in 200 cc. of dry carbon tetrachloride. The material which remained after removal of excess bromine and solvent was distilled at 50 mm. The main fraction (4 g.) boiled at 68–70°. This boiling point is much lower than that of allene tetrabromide, which[11] is 115.5" at 9 mm. The index of refraction gave confirmatory evidence that it was propylene bromide. At 23.5" the value was 1.5178 as compared to the known value at 20° of 1.5182. Two or three drops of higher-boiling material had an index at 23° of 1.5420 and the same amount of residue in the flask had one of 1.5'720. The value for allene tetrabromide is 1.6200 at 20°. If the latter compound was not completely absent, it was certainly present in no more than traces.

After forty-eight hours' refluxing, the hot, sticky product was transferred as completely as possible to a Claisen flask equipped with a 20-cm. Vigreux column. The first fraction came over at 180–200° (atm. press.). Continuing at 23 mm., the next was collected from 100–123° and the third at 123°, constantly. The fractions weighed 2.8, 3.78 and 2.92 g., respectively. No more distillate could be obtained even when the flask was heated to 300° (23 mm.). While still hot, the residue was poured onto a watch glass. It solidified to form a brittle, black, resinous mass, weighing 18 g.

The three liquid fractions, with a total weight of 9.5 g., were separately treated with *p*-toluenesulfonyl chloride and alkali in the usual manner. The presence in them of 3.33 g. of aniline and 1.47 g. of allylaniline was established. The remainder was probably unchanged diallylaniline, to a certain extent. The identity of the derivatives with known samples was confirmed in each case.

Some work was done on the resinous material. About one-tenth of it was soluble in boiling 4 N hydrochloric acid. Neither the soluble nor the insoluble portion seemed to give quinones on oxidation with dichromate in dilute sulfuric acid solution. The molecular weight of the original resin in acetone was 783, an average of the values obtained from the following data.

Mol. wt. Subs., 2.1868 g.: vol. acetone taken, 26.0, 25.0, 26.5 cc.; *AT*, 0.255, 0.250, 0.235". Mol. wts.: found, 793, 777, 779.

Action of Acrolein on Aniline.—To a solution of 9.3 g. of aniline in 10 cc. of 95% alcohol and held at about 10° in an ice-bath, there was added slowly the theoretical amount (5.5 g.) of acrolein. The reaction was strongly exothermic, giving a slightly yellow, sticky mass. This was washed with petroleum ether, then dissolved in ether and precipitated from it by the addition of petroleum ether. The solvent was poured off. and as the solvent evaporated from the residue, the sticky mass gradually changed into

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[11] Hurd, Meinert and Spence, THIS JOURNAL, 52, 1145 (1930).

a slightly yellow powder. It started to soften and become dark colored at 68°, and melted at about 76°. Some of this material was heated at 150' for ten minutes. After cooling and solidifying, it then melted at 87°. This resin resembled in appearance the one which was formed in the pyrolysis of diallylaniline.

Diallyl-*p*-phenetidine

Synthesis.—To 50 g. of p-phenetidine in a balloon flask equipped with an air condenser was added 45 g. of allyl bromide in small portions. After being heated for fifteeen minutes on a water-bath, the mixture was made alkaline and extracted with ether. The solvent was evaporated from the dried ether extract and to the residue was added another 45-g. portion of allyl bromide, The mixture was heated on a boiling water-bath for fifteen minutes and allowed to stand overnight. It was made alkaline and ether-extracted. The extract was dried over stick potassium hydroxide, the ether evaporated and the residue distilled from a modified Claisen flask at 23 mm. The distillate boiling at 162–170° was 60 g., or 76% of the caculated amount. Redistillation gave 50 g. of pure material boiling at 164–165°. Its density, d_4^{23}, was 0.9921, and its index of refraction, n_D^{22}, 1.5458.

Anal. (Kjeldahl). Subs., 0.3456, 0.3594: cc. of 0.1311 *N* HCl, 12.46, 12.80. Calcd. for $C_{14}H_{19}ON$: N, 6.45. Found: N, 6.62, 6.55.

Preparation of *p*-Toluenesulfone-*p*-phenetidide.—A mixture of 7.8 g. of *p*-phenetidine, 19 g. of *p*-toluenesulfonyl chloride and 100 cc. of 2 *N* potassium hydroxide was allowed to stand overnight and was worked up in the customary manner. The treatment with sodium ethoxide must not be omitted. Altogether, there was obtained 13.4 g. of product, an 81% yield. Crystallization from methanol, accompanied by treatment with bone black, gave beautiful colorless crystals, melting at 109° (110°, corr.).

Anal. Subs., 0.5244, 0.5381: cc. of 0.1311 *N* HCl, 13.20, 14.04. Calcd. for $C_{15}H_{17}O_3NS$: N, 4.81. Found: N, 4.63, 4.80.

Pyrolysis of Diallyl-*p*-phenetidine.—A 30-g. sample of diallyl-*p*-phenetidine was heated in an all-glass apparatus in a fused salt bath. It refluxed at 265° with the evolution in seventeen minutes of 350 cc. of gas. Analysis showed this to be 95% propylene, 0.4% ethylene, 1.3% oxygen and 3.3% nitrogen. The remaining gas was led into 200 cc. of carbon tetrachloride which contained 18 g. of bromine. Identification of the major portion as propylene and not allene was accomplished as outlined above for the gas from diallylaniline. Distillation of the bromide derivative at 25 mm. gave 1.5 g. at 48–50''; its index of refraction was 1.5180. Practically complete distillation of the material remaining in the flask gave 1.75 g. with an index of 1.5225. The value for propylene dibromide at 20° is 1.5182, while that for allene tetrabromide is 1.6200. Furthermore, the boiling point of the latter compound is 115.5° at 9 mm., which is much higher than the value of the material in question.

After forty-four hours of refluxing, the hot contents of the reaction vessel were transferred to a modified Claisen flask and distilled at 25 mm. In the range of 139–146° there was obtained 7.9 g. of *p*-phenetidine, identified as *p*-toluenesulfone-*p*-phenetidide in a yield equivalent to that which was obtained from a sample of the pure amine. The melting point was 109° and this was unchanged by admixture of known material. Additional proof of the identity of the material as p-phenetidine was secured by diazotization, replacement by a cyanide group, and hydrolysis of the latter to *p*-ethoxybenzoic acid, m. p. 197°. From 146–165° was obtained 1.5 g., containing 0.9 g. of p-phenetidine. The brittle black resin which remained as a distillation residue weighed 17 g.

In brief, 30 g. of diallyl-*p*-phenetidine on refluxing at 276–272'' for forty-four hours gave 8.8 g. of phenetidine, 1.35 g. of propylene (0.61 g. in 350 cc. of gas, and 0.74 g.

equivalent to 3.25 g. of the dibromide), 17 g. of resin, and 2.85 g. lost or unidentified. A weight of propylene that would be equivalent (2 moles) to the phenetidine formed would be 3.24 g. No monoallylphenetidine was found. Its stability at the reflux temperature of 275° is evidently less than that of allylaniline at 240°.

Pyrolysis. Two Hours of Reflux. —A 30-g. sample of diallyl-p-phenetidine on refluxing for two hours in an all-glass apparatus gave 10.6 g. of liquid products, 16.5 g. of resin and 2.65 g. of propylene. The phenetidine in the liquid products amounted to 8.07 g. These results are almost identical with those obtained with the forty-four hours reflux period. The greater recovery of propylene in this instance is due to the fact that the gas was collected as such and was not subjected to the unavoidable losses occasioned by its conversion into propylene dibromide.

Summary

The behavior of allylaniline, diallylaniline and diallyl-p-phenetidine at elevated temperatures has been studied. In general, the products are the parent primary amine, propylene and resinous material. Some quinoline was formed from allylaniline at 700°. Allene was not a product of the pyrolysis. Mechanisms have been suggested and discussed.

The following new compounds have been prepared and characterized: diallyl-p-phenetidine, allyl-*p*-toluenesulfonanilide and *p*-toluenesulfone-*p*-phenetidide.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE INSECTICIDE DIVISION. BUREAU OF CHEMISTRY AND SOILS]

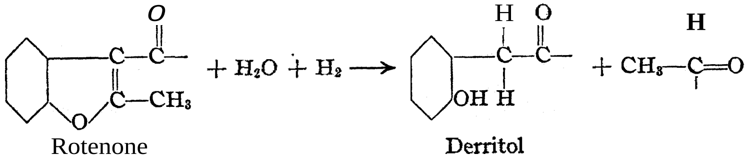
ROTENONE. X. CLEAVAGE OF DERRITOL AND ROTENOL

BY **L. E. SMITH** AND F. B. LAFORGE

RECEIVED SEPTEMBER 24, 1930 PUBLISHED NOVEMBER 5, 1930

When rotenone, $C_{23}H_{22}O_6$, is boiled with zinc dust and potassium hydroxide in alcoholic solution, two products are obtained: derritol, a yellow phenol formed with the loss of two carbon atoms, and a white compound, rotenol,[1] which contains two hydrogen atoms more than rotenone and which exhibits the properties of an alcohol.

Butenandt[1] has advanced several theories to account for the formation of derritol of which the following mechanism is an example



Rotenone Derritol

Rotenol is assumed by the same author to be formed by the reduction of the carbonyl group of rotenone to a secondary alcohol group.

In previous articles[2,3] we have reported that several compounds derived

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[1] Butenandt. *Ann.*, 464, 253 (1928).

[2] La Forge and Smith, THIS JOURNAL, **52**, 1091 (1930).

[3] La Forge and Smith, *ibid.*, **52**, 3603 (1930).

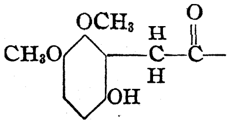
from dehydrorotenone are cleaved by hydrogen peroxide in alkaline solution to dibasic acids which contain the original two methoxy groups present in rotenone. Derric acid of formula $C_{12}H_{14}O_7$ was obtained from hydroxyrotenonic, as well as from dihydroxyrotenonic acids, while dehydrorotenonic acid gave the next lower homolog of derric acid, $C_{11}H_{12}O_7$, the latter acid being identical with the permanganate oxidation product of derric acid.

Both derritol and rotenol, as already reported,[4] yield acids on catalytic hydrogenation although in the case of derritol it is found convenient to methylate the phenol group in order to facilitate separation of the dihydroderritol and derritolic acid. In the case of rotenol the original double bond in the side chain of rotenone is also reduced during hydrogenation to the acid. The two resulting compounds, methylderritolic and dihydrorotenolic acids, are both well adapted to oxidation by the alkaline peroxide method and both yield interesting cleavage products.

Methylderritolic acid yields a monobasic trimethoxy acid of formula $C_{11}H_{14}O_5$ corresponding to a trimethoxyphenylacetic acid. Permanganate oxidation of this compound yields the next lower homolog, an acid of formula $C_{10}H_{12}O_5$, still containing the three methoxyl groups, and in all probability, a trimethoxybenzoic acid. Of the six theoretically possible compounds of this nature, four are known, but the properties of the compound obtained from derritol do not correspond to those of any of them. There remain the 2,3,5- and 2,3,6-trimethoxybenzoic acids of which the new compound most likely corresponds to the last-mentioned derivative. The choice between the two possibilities must be decided by synthesis of one or both of the missing members.

It follows from the facts so far established that the phenolic hydroxyl group in derritol arises from the indifferent oxygen atom in rotenone, that this group is attached to the same benzene nucleus as the methoxyl groups and that at least one carbon atom separates that nucleus from the carbon atom, probably the carbonyl group, at which cleavage takes place.

It seems probable therefore that derritol does in fact contain the grouping (A) as suggested by Butenandt.[1]



A

As mentioned above, dihydrorotenolic acid is easily cleaved by alkaline peroxide and in this case also a monocarboxylic acid is obtained in good yield.

The acid obtained from rotenol is represented by the formula $C_{12}H_{14}O_5$. It contains the original two methoxyl groups of rotenone, gives no test for a phenol and does not reduce Fehling's solution. The compound will be named netoric acid.

Oxidation of Methylderritolic Acid with Hydrogen Peroxide.—The procedure followed in carrying out this reaction was the same as that used for the preparation of derric

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[4] La Forge and Smith, THIS JOURNAL, 52, 1088 (1930).

acid.[5] Two grams of methylderritolic acid[4] was dissolved in 25 cc. of 5% potassium hydroxide. The solution was warmed to 60° and 6 cc. of 30% hydrogen peroxide was added in small portions, after which the solution was boiled to remove any excess hydrogen peroxide. After cooling, the solution was made acid with dilute hydrochloric acid and extracted with ether. The ether solution was dried over anhydrous sodium sulfate and the ether evaporated. The residue crystallized at once. The oily by-products were removed by pressing the crystals between filter papers, after which the compound was recrystallized from water. The melting point was 93°; the yield, 0.7 g. Owing to the presence of water of crystallization, the substance was dried for analysis to constant weight at 110°.

Anal. Subs., 0.0740, 0.0772: CO_2, 0.1578, 0.1650; H_2O, 0.0411, 0.0423. Subs., 0.0218, 0.0143: AgI, 0.0676, 0.0455. Calcd. for $C_{11}H_{14}O_5$: C, 58.40; H, 6.15; $3CH_3O$: 41.4. Found: C, 58.16, 58.25; H, 6.16, 6.10; CH_3O, 40.96, 42.02. *Titration.* Subs., 0.0194: 0.905 cc. of $N/10$ KOH. Calcd. mol. wt.: 226. Found: 214.

Oxidation of Acid of Formula $C_{11}H_{14}O_5$ (Trimethoxyphenylacetic Acid).—Three-tenths of a gram of the acid was dissolved in 50 cc. of water containing an excess of potassium hydroxide and to the cold solution 0.45 g of potassium permanganate dissolved in 50 cc. of water was added in small portions. When the purple color had disappeared, the solution was warmed on the steam-bath and filtered. After evaporation to a small volume the solution was acidified and extracted with ether and the ether solution dried over anhydrous sodium sulfate. After removal of the solvent the residue was distilled in a high vacuum. The distillate crystallized at once and was recrystallized from carbon tetrachloride. The melting point was 78–80°; the yield. 0.14 g. For analysis the substance was dried to constant weight at 110".

Anal. Subs., 0.0737, 0.0766: CO_2, 0.1530, 0.1593; H_2O, 0.0404, 0.0434. Calcd. for $C_{10}H_{12}O_5$: C, 56.6; H, 5.66. Found: C, 56.62, 56.70; H, 6.09, 6.29. *Titration.* Subs., 0.0195: 1.76 cc. $N/20$ KOH. Calcd. mol. wt.: 212. Found: 221.

Amide.—One-half gram of the acid was dissolved in 12 cc. of dry benzene and 0.5 g of phosphorus pentachloride was added. The solution was gently boiled until all of the hydrochloric acid was removed, then cooled in an ice-bath and dry ammonia gas passed into the solution. Water was then added and the benzene boiled off. The amide crystallized from the aqueous solution and was recrystallized from the same solvent. The melting point was 173° and the yield, 0.35 g. The compound was analyzed for nitrogen by the micro Kjeldahl method.

Anal. Subs., 0.0171: 0.76 $N/10$ HCl. Calcd. for $C_{10}H_{13}O_4N$: N. 6.63. Found: N, 6.46.

Oxidation of Dihydrorotenolic Acid.—The procedure followed in this reaction was also the same as that used for the preparation of derric acid.[5] Two grams of dihydrorotenolic acid[4] was dissolved in 25 cc. of 5% potassium hydroxide, the solution warmed to 60° and 6 cc. of 30% hydrogen peroxide was added in small portions. With each addition of hydrogen peroxide the solution was stirred until the precipitate which formed was dissolved. When the solution began to effervesce the stirring was discontinued. The reaction mixture was then boiled to remove excess peroxide and the small amount of separated resinous material extracted with ether. The solution was then acidified with dilute hydrochloric acid and extracted with ether. After drying over anhydrous sodium sulfate the ether was removed, leaving a sirupy residue which soon crystallized. The adhering oil was removed by pressing between filter papers. The compound was then recrystallized from water. The substance contained crystal water, and for an-

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[5] La Forge and Smith, THIS JOURNAL, 52, 2878 (1930).

alysis was dried to constant weight at 110°. The melting point was 91–92°. The yield was 0.5 g.

Anal. Subs., 0.0734, 0.0638: H_2O, 0.0055, 0.0044. Calcd. for $C_{12}H_{14}O_5{\cdot}H_2O$: H_2O, 7.04. Found: 7.4, 6.9. Subs., 0.0594, 0.0679; CO_2, 0.1318, 0.1515; H_2O, 0.0316, 0.0351. Subs., 0.0200, 0.0199: AgI, 0 0392, 0.0391. Calcd. for $C_{12}H_{14}O_5$: C, 60.50; H, 5.88; $2CH_3O$, 26.05. Found: C, 60.49, 60.84; H, 5.91, 5.74; CH_3O, 25.89, 25.95. *Titration.* Subs., 0.0201: 1.72 cc. $N/20$ KOH. Calcd. mol. wt.: 238. Found: 234. 0.1982 g. of subs. in 10.6 cc. of ethyl alcohol showed no appreciable rotation in a 2-dm. tube.

Summary

Methylderritolic acid yields on alkaline peroxide oxidation a monocarboxylic acid of formula $C_{11}H_{14}O_5$ having the properties of a trimethoxyphenylacetic acid which yields the next lower homolog by permanganate oxidation. The new acid corresponds in its empirical formula to a trimethoxybenzoic acid but does not agree in its properties with any of the four known compounds of this type. It therefore probably corresponds to either the 2,3,5- or 2,3,6-derivative, both of which are unknown.

Dihydrorotenolic acid on peroxide oxidation yields a monocarboxylic acid of formula $C_{12}H_{14}O_5$ containing the two methoxyl groups of rotenol.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

ON THE COURSE OF ADDITION OF SODIUM ENOL ALKYL MALONIC ESTERS TO ALPHA, BETA-UNSATURATED ESTERS

BY ARTHUR MICHAEL AND JOHN ROSS

RECEIVED OCTOBER 6, 1930 PUBLISHED NOVEMBER 5, 1930

In the first account of the addition of sodium enol malonic ester to esters of α,β-unsaturated acids[1] the reaction was expressed as though the parts of the addendum were Na and $-CH(COOEt)_2$

$$\begin{array}{lcl} \mathrm{RCH{=}CHCOOEt} & & \mathrm{RCHCHNaCOOEt} \\ + & \longrightarrow & | \\ \mathrm{NaCH(COOEt)_2} & & \mathrm{HC(COOEt)_2} \end{array}$$

In agreement with this view, the many cases of α,β-olefinic carboxylic esters that have since been examined by reaction with sodium enol malonic ester gave products that indicated that the malonic residue had united with the 8-carbon atom. After the enol structure was assigned *to* the sodium derivative of malonic ester[2] the above reaction continued to be written as though the sodium atom migrated in the reaction.[3] This mecha-

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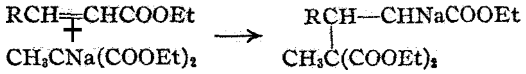
[1] Michael, J. *prakt.* Chem., 35, 349 (1887).

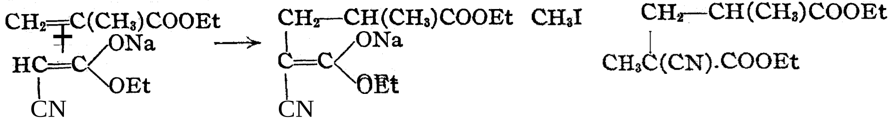
[2] Michael, *ibid.*, 37, 496 (1889).

[3] Although usually written as though the sodium atom becomes attached to the a-carbon atom of the unsaturated ester, attention had been called to the fact that the structure of such an addition compound would be unstable and would rearrange from the $-CHNaCOOEt$ to the $-CH{=}C(ONa)OEt$ form [Michael, Ber., 33, 3731 (1900)].

nism for the reaction received apparent support when it was shown that addition products could be obtained using sodium enol alkyl malonic esters in the place of sodium enol malonic ester.[4]

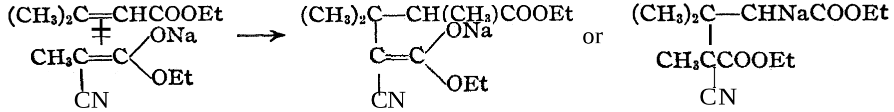


J. F. Thorpe[6] examined the reaction of the sodium derivatives of cyanacetic and of a-cyanopropionic esters and concluded that the above manner of expressing the addition of sodium enol malonic esters to α,β-unsaturated esters was erroneous. He showed that the addition of sodium enol cyanacetic ester to a-methylacrylic ester proceeded as follows, since upon treating with methyl iodide the addition compound gave α,γ-dimethyl-γ-cyano glutaric ester

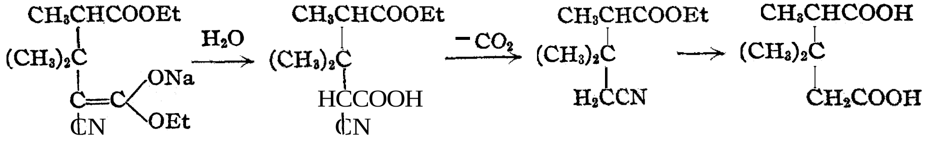


Thorpe regarded this as evidence that the sodium showed no tendency to leave the oxygen in the more acidic cyanacetic ester residue in order to add to the α-carbon atom attached to only one carbethoxyl group, and concluded that the reaction took place with migration of hydrogen but not of sodium.

In the addition of sodium enol a-cyanopropionic ester to β,β-dimethyl acrylic ester, the following possibilities were considered



The acid cyano ester obtained upon acidifying the product lost carbon dioxide upon distillation to give a cyano ester. This upon hydrolysis yielded α,β,β-trimethylglutaric acid and it was, therefore, concluded, that the methyl group had migrated to the a-carbon atom in the initial addition. These reactions were expressed as follows



Michael[6] examined the addition of sodium enol methylmalonic ester to crotonic ester and obtained an ester (a) which upon treatment with methyl

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[4] Auwers, *Ber.*, *24*, 307, 1923, 2887 (1891).

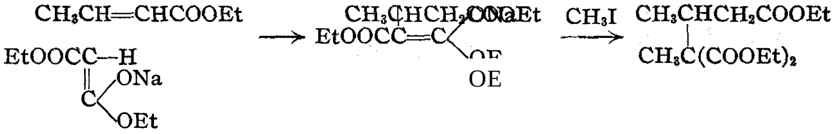
[5] Thorpe, *J. Chem. Soc.*, 77,923 (1900).

[6] Michael, *Ber.*, 33, 3731 (1900).

iodide gave a quantitative yield of a trimethylcarboxyglutaric ester. Methylation of the sodium derivative of 8-methyl-y-carboxyglutaricester (prepared by addition of sodium enol malonic ester to crotonic ester) gave a dimethyl y-carboxyglutaric ester (b), which had quite different properties from the isomeric ester (a). The ester (a) not only boiled 6° lower than the ester (b) but upon attempted methylation with sodium ethoxide and methyl iodide the ester (b) gave crotonic and dimethylmalonic esters. Evidently ester (a) forms a stable sodium derivative whereas ester (b) does not, but undergoes retrogression into crotonic and sodium enol methyl malonic esters.[7] From their methods of preparation the two esters should have been identical and Michael was unable to explain the appearance of different compounds. Thorpe's research appeared at about the same time but neither chemist was aware of the other's work.

In view of these anomalous results it was decided to reexamine the addition of sodium alkyl malonic esters to α,β-unsaturated esters and determine the constitution of the two isomeric esters (a) and (b). It was thought that this might lead to an explanation of the reactions by which they were formed.

When the product of addition of sodium enol malonic ester to crotonic ester is treated with methyl iodide, β,γ-dimethyl-γ-carboxyglutaric ester is formed



This is a proof that when sodium enol malonic ester is used in these addition reactions, then the sodium remains combined with the oxygen in the malonic residue. In other words, the addendum components are H and —C(COOEt)=C(ONa)OEt, a parallel mechanism shown by Thorpe to occur with sodium enol cyanacetic ester addition. It has also been shown that it is hydrogen that migrates in the reactions of sodium enol malonic, sodium enol alkyl malonic esters[8] and diethylaminocrotonic ester[9] toward phenyl isocyanate.

If the above conception of the mechanism of this reaction offers any parallel in the case of the addition of sodium enol alkyl malonic esters to such α,β-unsaturated esters, the course of the reaction would depend upon the chemical hindrance to separation of the components of the addendum, that is, upon the separation of the alkyl group from the directly attached carbon atom. This might be rendered possible by the positive character

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[7] This was the first proof of the possible retrogression of these addition reactions; the subject was later more fully investigated by Ingold, *J. Chem. Soc.*, **119, 1976 (1921)**.

[8] Michael, *Ber.*, 37, 32 (1905).

[9] Michael and Cobb, *Ann.*, 363, 14 (1905).

ture was acidified and from the precipitated material was separated the derivative of the primary amine by solution in boiling 10% alkali in the usual way. The alkali-insoluble material was treated with sodium ethoxide to convert any disulfonyl derivatives of primary amines to the monosulfonyl ones. The *p*-toluenesulfonyl derivatives were, in general, purified by crystallization from methanol and water. Filter charcoal was used if necessary. The yields obtained from known quantities of the amines concerned were considered in determining the composition of mixtures by this plan.

Allylaniline

Synthesis.—Allylaniline was prepared in yields of about 30% by the action of allyl bromide on sodium acetanilide. After subsequent hydrolysis, the product was purified by vacuum distillation. Its boiling point was 115° at 23 mm. and 218° at 745 mm. The material contained about 2% of aniline by analysis. It was not found practicable to form allylaniline by the action of equimolar quantities of aniline and allyl bromide as Schiff[10] recommended.

Pyrolysis at 275°.—A sample of material containing 12.15 g. of allylaniline and 0.35 g. of aniline was heated in a sealed tube at 275° for twelve hours. A small amount of inflammable gas was noticed when the tube was opened. Distillation at atmospheric pressure gave 2.5 g. at 186–206°, 3.0 g. at 206–220°, 2.5 g. at 220–223° and a residue of 3.9 g. of black, viscid tar. not volatile even under reduced pressure. The three fractions were treated separately with *p*-toluenesulfonyl chloride and excess alkali. The presence in them of 1.38 g. of aniline and 6.24 g. of allylaniline was established. The identity of the derivatives obtained was verified in each case by the melting point and a mixed melting point with authentic specimens. The aniline derivative melted at 103° and its melting point was not lowered by admixture of known *p*-toluenesulfonanilide. Allyl-p-toluenesulfonanilide melted at 69° and a mixed m. p. had the same value.

Pyrolysis at 600°.—Allylaniline was dropped very slowly into a 50-cc. distilling flask held at 270°. The vapor thus formed was conducted through a horizontal pyrex tube heated to 600° in a gas combustion furnace, The temperature, as indicated by a chromel–alumel thermocouple potentiometer set-up, did not vary from this temperature by more than three degrees. A bent piece of smaller tubing, sealed to the exit end of the reaction tube, extended into a 25-cc. distilling flask. The latter was cooled in an ice–salt bath. A U-tube, in series with the flask and held at the same temperature, collected nothing. The residual gas was collected over water in a 2.5-liter bottle.

A 14-g. sample of allylaniline was passed through the apparatus in three hundred and fifty minutes. The dimensions of the tube and the barometric pressure were such that the contact time in the hot zone was 154 seconds. The amount of liquid product was 10.1 g. The gas collected was about 1300 cc. (0°, 760 mm.). It gave on analysis in percentage by volume: propylene 28.1, ethylene 12.9, hydrogen 9.4, carbon monoxide 2.8, paraffins 36.2 (n in C_nH_{2n+2} was 1.68), nitrogen 11.6. As would be expected under these conditions, much of the propylene which was formed underwent pyrolysis. Considerable carbonization and the presence of hydrogen cyanide in the off-gases were indicative of secondary reactions. Hydrogen cyanide was tested for by passing the gas through water in a test-tube and converting it into Prussian blue. Thus, alkali was added, then ferrous and ferric ions. On boiling for a minute and then acidifying, the blue precipitate appeared.

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[10] Schiff, Ann. *Supplement,* 3, 364 (1864).

The liquid product was fractionated. Below 105° was obtained 0.5 g., which was presumably benzene. At 105–190° but mostly at 180–186° was collected 4.25 g. of liquid, 3.44 g. of which was confirmed as aniline through p-toluenesulfonanilide. Three grams of distillate containing 1.53 g. of aniline was collected at 120–150° and 70 mm. Summarizing, a sample of material containing 13.61 g. of allylaniline and 0.39 g. of aniline gave 4.97 g. of aniline, about 0.5 g. of benzene, 2.35 g. of non-distillable tar, and 2.28 g. of unidentified liquids. The 1300 cc. of gas contained propylene and its decomposition products. No unchanged allylaniline was found.

Pyrolysis at 700°.—During sixty-four minutes a 50-g. sample of allylaniline was displaced by mercury from a graduated capsule into a vertical pyrex tube. This tube was heated to 700° in an electric furnace whose temperature was automatically controlled and recorded by a Leeds–Northrup potentiometer type recorder-controller. The dimensions of the hot part of the reaction tube were 90 × 2.1 cm. and the contact time was calculated to be thirty-nine seconds. A small tube sealed to the main reaction tube passed into a 100-cc. distilling flask which was surrounded by an ice–salt bath. The products which condensed in this flask weighed 44 g. A U-tube in series with it and also cooled by ice–salt collected nothing. The gases of the reaction, collected over water at 21° and 740 mm., had a volume of 6.5 liters. The corrected volume was 5.7 liters.

The liquid product was fractionally distilled. The first fraction was collected at 740 mm. between 80–150°, mostly below 120°. This material was identified as benzene by conversion into m-dinitrobenzene, m. p. 87°; mixed m. p. 89°. The distillation was continued at 24 mm. The greater part of an 80–90° fraction weighing 19.7 g. came over at 87–88". Of this, 15.7 g. was identified as aniline through conversion of a portion into p-toluenesulfonanilide. In the range of 90–200°, 11.5 g. of a deep yellow liquid was obtained; non-volatile residue, 8 g. Of the 11.5 g. of distillate, 3.4 g. was identified as aniline. Only a trace of secondary amine was present. The presence of 1–2 g. of quinoline in this fraction was established as follows. The tertiary amines in 2.27 g. of the distillate were separated, employing *p*-toluenesulfonyl chloride in the usual way. After steam distillation, ether extraction and evaporation of the ether, methyl iodide was added and the mixture allowed to stand for two to three hours. The solid obtained was crystallized from 3 cc. of absolute alcohol. The yellow crystals were pressed on a porous plate. They melted at 73°, the melting point of quinolinium methiodide. The mixed melting point with an authentic specimen was also 73°.

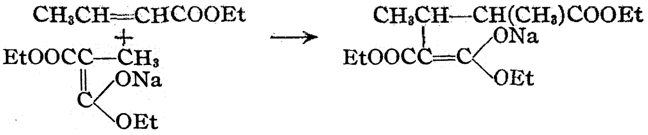
The analysis of the gas was as follows: CO_2, 0.7; unsatd. hydrocarbons soluble in 62.5% H_2SO_4, 1.3; propylene, 24.0; ethylene, 18.1; oxygen (from admixed air), 4.9; hydrogen, 15.9; CO, 0.6; residue of paraffins and nitrogen, 34.5.

Allyl-*p*-toluenesulfonanilide.—Allylaniline was treated with 1.5 equivalents of *p*-toluenesulfonyl chloride and 4–5 equivalents of 2 N potassium hydroxide. The mixture was allowed to stand overnight, acidified and worked up in the usual way. The yield was 75% and the melting point was 69°, or 69.3° corrected. An identical product was obtained in 89% yields by the action of an excess of allyl bromide on p-toluenesulfonanilide in *N* alkali solution. This method is preferable because of the difficulty in obtaining allylaniline. Unused p-toluenesulfonanilide was removed by solution in hot 2 *N* potassium hydroxide solution.

Anal. (Kjeldahl). Subs., 0.5155, 0.5437, 0.5329: cc. of 0.1311 N HCl, 13.68, 14.38. 14.00. Calcd. for $C_{16}H_{17}O_2NS$: N, 4.88. Found: N, 4.87, 4.83, 4.83.

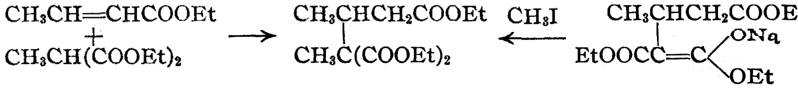
Diallylaniline

Preparation.—This was prepared in 68% yield by the action of allyl bromide on residues from the attempted direct preparation of allylaniline. The boiling point of of the alkyl group and the strong positive influence of the slightly neutralized sodium atom in loosening the affinity between the respective carbon atoms. The addendum to the ethylenic linkage would then be alkyl and —C(COOEt)=C(ONa)OEt. With sodium enol methylmalonic ester and crotonic ester the reaction would be as follows



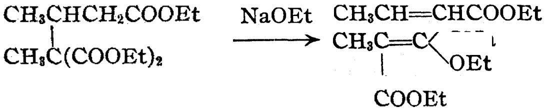
$$\begin{matrix} CH_3CH{=}CHCOOEt \\ + \\ EtOOCC{-}CH_3 \\ \| \\ C(ONa)OEt \end{matrix} \longrightarrow \begin{matrix} CH_3CH{-}CH(CH_3)COOEt \\ | \\ EtOOCC{=}C(ONa)OEt \end{matrix}$$

Upon examining the conditions of addition of methylmalonic to crotonic ester, it was found that the course of the reaction varied according to the amount of sodium ethoxide used. When the addition was carried out in the presence of a small quantity of sodium ethoxide, then the addendum functioned as H and —$C(CH_3)(COOEt)_2$. With one-sixth of a molecular equivalent of sodium ethoxide, almost the theoretical yield of β,γ-dimethyl-γ-carboxyglutaric ester was obtained. This ester is also 60% of the product of methylation of the sodium derivative of β-methyl-γ-carboxyglutaric ester with methyl iodide. These reactions may be represented thus



$$\begin{matrix} CH_3CH{=}CHCOOEt \\ + \\ CH_3CH(COOEt)_2 \end{matrix} \longrightarrow \begin{matrix} CH_3CHCH_2COOEt \\ | \\ CH_3C(COOEt)_2 \end{matrix} \xleftarrow{CH_3I} \begin{matrix} CH_3CHCH_2COOEt \\ | \\ EtOOCC{=}C(ONa)OEt \end{matrix}$$

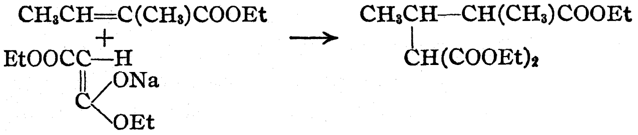
In each case the structure of the ester was proved by saponifying and isolating the β,γ-dimethyl-γ-carboxyglutaric acid, m. p. 167°. Furthermore, it was shown that β,γ-dimethyl-γ-carboxyglutaric ester would not form a sodium derivative. Upon attempted methylation by treatment in the cold with sodium ethoxide and methyl iodide, fission occurred into crotonic and sodium enol methylmalonic esters.



$$\begin{matrix} CH_3CHCH_2COOEt \\ | \\ CH_3C(COOEt)_2 \end{matrix} \xrightarrow{NaOEt} \begin{matrix} CH_3CH{=}CHCOOEt \\ CH_3C{=}C(OEt) \\ | \\ COOEt \end{matrix}$$

The sodium enol methyl malonic ester was converted by the methyl iodide into dimethylmalonic ester.

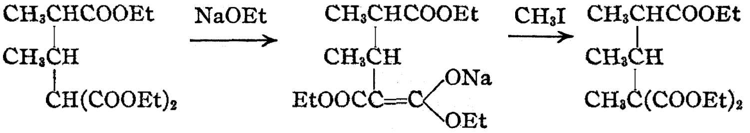
When methylmalonic ester and crotonic ester were condensed using a molecular equivalent of sodium ethoxide, no β,γ-dimethyl-γ-carboxyglutaric ester was formed. Instead, a 60% yield of α,β-dimethyl-γ-carboxyglutaric ester was obtained. Hence it is concluded that under these conditions the reaction takes place with migration of the methyl group. The direct proof of this migration of the methyl group was obtained by comparison of the α,β-dimethyl-γ-carboxyglutaric acid, m. p. 145°, obtained on saponification of the above ester, with the acid synthesized by the addition of sodium enol malonic ester to tiglic ester as follows.



$$\begin{array}{l}\mathrm{CH_3CH{=}C(CH_3)COOEt} \\ \quad + \\ \mathrm{EtOOCC{-}H} \\ \quad \| \\ \quad \mathrm{C}\begin{matrix}\mathrm{ONa} \\ \mathrm{OEt}\end{matrix}\end{array} \longrightarrow \begin{array}{l}\mathrm{CH_3CH{-}CH(CH_3)COOEt} \\ \quad | \\ \mathrm{CH(COOEt)_2}\end{array}$$

However, the yields are small by this method (about 15%). Blaise[10] prepared α,β-dimethyl-γ-cyanoglutaric ester by addition of sodium enol cyanacetic ester to tiglic ester and obtained a better yield (65%). He also obtained α,β-dimethyl-γ-carboxyglutaric acid from the above cyano ester, but described it as a thick sirup. Repeating his synthesis, a crystalline acid was obtained which was identical with the acid prepared by the other methods.

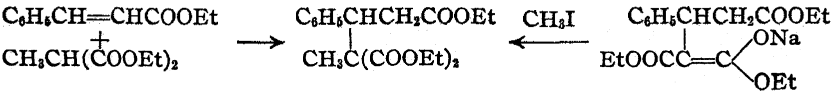
The α,β-dimethyl-γ-carboxyglutaric ester readily gave a sodium derivative which with methyl iodide gave the theoretical yield of α,β,γ-trimethyl-y-carboxyglutaric ester



$$\begin{array}{l}\mathrm{CH_3CHCOOEt} \\ \quad | \\ \mathrm{CH_3CH} \\ \quad | \\ \mathrm{CH(COOEt)_2}\end{array} \xrightarrow{\mathrm{NaOEt}} \begin{array}{l}\mathrm{CH_3CHCOOEt} \\ \quad | \\ \mathrm{CH_3CH} \\ \quad | \\ \mathrm{EtOOCC{=}C}\begin{matrix}\mathrm{ONa} \\ \mathrm{OEt}\end{matrix}\end{array} \xrightarrow{\mathrm{CH_3I}} \begin{array}{l}\mathrm{CH_3CHCOOEt} \\ \quad | \\ \mathrm{CH_3CH} \\ \quad | \\ \mathrm{CH_3C(COOEt)_2}\end{array}$$

When β,γ-dimethyl-γ-carboxyglutaric ester was treated with one molecular equivalent of sodium ethoxide, about half underwent retrogression into crotonic and methylmalonic esters. The remainder was converted into α,β-dimethyl-γ-carboxyglutaric ester, while a small amount (about 5%) of the ester was recovered unchanged. Since the addition is readily reversible, the change from β,γ-dimethyl-γ-carboxyglutaric ester to α,β-dimethyl-γ-carboxyglutaric ester undoubtedly went through this stage, the methyl migrating by virtue of the type of addition that occurs between the sodium enol methylmalonic and crotonic esters.

Parallel results were obtained in the addition of sodium enol methyl malonic ester to cinnamic ester. When the condensation was carried out using one-fifth of a molecular equivalent of sodium ethoxide, y-methyl-@-phenyl-γ-carboxyglutaric ester was produced, showing that the parts of the addendum under these conditions are H and $\mathrm{{-}C(CH_3)(COOEt)_2}$. The same ester was obtained by treatment of the sodium derivative of β-phenyl-γ-carboxyglutaric ester with methyl iodide



$$\begin{array}{l}\mathrm{C_6H_5CH{=}CHCOOEt} \\ \quad + \\ \mathrm{CH_3CH(COOEt)_2}\end{array} \longrightarrow \begin{array}{l}\mathrm{C_6H_5CHCH_2COOEt} \\ \quad | \\ \mathrm{CH_3C(COOEt)_2}\end{array} \xleftarrow{\mathrm{CH_3I}} \begin{array}{l}\mathrm{C_6H_5CHCH_2COOEt} \\ \quad | \\ \mathrm{EtOOCC{=}C}\begin{matrix}\mathrm{ONa} \\ \mathrm{OEt}\end{matrix}\end{array}$$

These esters were identified by the acids obtained from them upon saponification. Two apparently stereomeric forms of γ-methyl-β-phenyl-γ-carboxyglutaric acid were obtained, m. p. 148 and 188°, respectively. The

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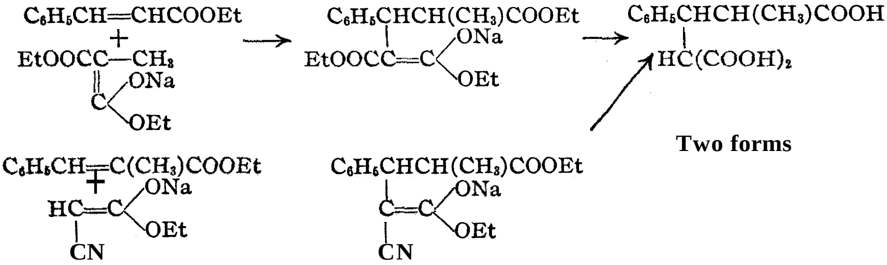
[10] Blaise, *Bull. soc. chim.*, [3] *29*, 332 (1903).

acid of m. p. 148° is a labile form and under certain conditions changes into the stable form, m. p. 188°. However, the acid of m. p. 148°, crystallized in large prisms, could be kept apparently for an indefinite period (a specimen over six months old shows no signs of change). Such isomerism in an acid of the glutaric series, asymmetric about one carbon atom only, is anomalous since a meso as well as a racemic form is not possible,

When methyl malonic ester was added to cinnamic ester, using one molecular equivalent of sodium ethoxide, the addition product consisted entirely of α-methyl-β-phenyl-γ-carboxyglutaric ester. Upon saponification and separation of the isomeric acids produced from this ester, two apparently stereomeric forms of **a-methyl-fl-phenyl-y-carboxyglutaric** acid were obtained. These were identified by direct comparison with the isomeric acids synthesized from the condensation product of sodium enol cyanacetic ester with α-methylcinnamic ester. The α-methyl-β-phenyl-γ-carboxyglutaric acid was obtained by hydrolysis of the cyano ester with caustic potash.



From these experiments it is apparent that sodium enol methylmalonic ester will suffer fission in the presence of an α,β-unsaturated ester so that the addendum to the ethylenic carbon atoms becomes CH_3 and $-C(COOEt)-$ $=C(ONa)OEt$. When small amounts of sodium ethoxide are used to bring about the addition of methylmalonic ester to unsaturated esters, an entirely different mechanism is involved and the sodium enol methylmalonic ester cannot be considered to react as such; it is even doubtful whether it is formed. The small amount of sodium methoxide merely serves as a catalyst in the same manner as certain nitrogen bases, *e.* g., piperidine, diethylamine,[11] used to produce similar additions of malonic to unsaturated esters.

A reacting system will proceed along the course whereby the maximum possible degradation of energy under the conditions of the experiment will be realized. This is illustrated by the conversion of maleic into fumaric acid by the catalytic action of a small amount of hydrobromic acid.[12] It may be assumed that a polymolecule of hydrobromic and maleic acid

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[11] Knoevenagel and Mottek, *Ber.*, 37,4464 (1904).

[12] Michael, Am. Chem. *J.*, 39, 3 (1908).

is first formed, evidently possessing greater free chemical energy than maleic acid, which enables it upon decomposition to form fumaric acid with liberation of heat and hydrogen bromide. Such a transformation proceeds until almost all the maleic acid is converted into fumaric acid. Thus a far greater degradation of energy is realized in the formation of fumaric acid than would be achieved in the formation of a small amount of bromosuccinic acid. When a considerable quantity of hydrobromic acid reacts with maleic acid, a mixture of bromosuccinic with furnaric acid is obtained.

Similarly, small amounts of sodium ethoxide may form polymolecules of high free chemical energy content but low stability, with the alkyl malonic ester present. The maximum degradation of energy is accomplished by causing simple addition of the alkyl malonic ester to the unsaturated ester, rather than the formation of some sodium enol alkyl malonic ester and addition of this to the unsaturated ester with migration of alkyl group to form a small amount of the sodium enol derivative of the tricarboxylic ester.

However, when a molecular equivalent of sodium ethoxide is used, the neutralization of the sodium in the sodium enol alkyl malonic ester becomes the deciding energy factor upon the course of the reaction. This is realized by the migration of the alkyl radical and the consequent formation of a better neutralized sodium enol derivative.

As a consequence of the above results, it is very probable that the addition products obtained previously using sodium enol alkyl malonic esters are compounds in which the alkyl group has migrated from the malonic residue. Some of these compounds are under reexamination.

Experimental

β-Methyl-γ-carboxyglutaric ester was prepared by condensing sodium enol malonic ester with crotonic ester by Auwers.[13] A better yield was obtained by using a small amount of sodium ethoxide as condensing agent.

0.75 g. of sodium was dissolved in 10 cc. of absolute ethyl alcohol, 32 g. of malonic ester added and the mixture diluted with 300 cc. of dry ether; 23 g. of crotonic ester was added and the liquid refluxed for five hours on the water-bath. After cooling, a solution of 2 g. of acetic acid in 20 cc. of water was added with rapid shaking. The ethereal extract was washed with 10% sodium carbonate solution. The neutral ester had b. p. 144° (3 mm.); yield, 95%.

β-Methyl-γ-carboxyglutaric acid was obtained upon saponification of the above ester with 10% caustic soda. It crystallized in large prisms from a mixture of acetone and chloroform, m. p. 139°.

Anal. Calcd. for $C_7H_{10}O_6$: C, 44.21; H, 5.26. Found: C, 44.54; H, 5.36.

Methylation of **β-Methyl-γ-carboxyglutaric** Ester.—Two and three-tenths grams of sodium was pulverized and dissolved in 4.6 g. of ethyl alcohol in absolute ether solution by standing overnight;[14] 27.4 g. of β-methyl-γ-carboxyglutaric ester was added to the suspension of sodium ethoxide with cooling in ice and shaking. In a few minutes the

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[13] Auwers, *Ber.*, 24, 2888 (1891); Michael. ibid., 33, 3748 (1900).

[14] Brühl, ibid., 37, 2067 (1904).

sodium ethoxide went into solution and 15 g. of methyl iodide was added. After standing for six hours in ice water, the product was worked up in the usual fashion; 28 g. of ester, b. p. 160° (9 mm.), was obtained, representing almost the theoretical yield of dimethyl-y-carboxyglutaric ester.

Anal. Calcd. for $C_{14}H_{24}O_6$: C, 58.33; H, 8.33. Found: C, 58.2; H, 8.5.

β,γ-Dimethyl-γ-carboxyglutaric acid was obtained upon saponification of the above ester with caustic soda. It crystallized from acetone-chloroform mixture in characteristic nodules, m. p. 167°. Thorpe and Young[15] prepared this acid by methylation of β-methyl-γ-cyanoglutaric ester and give the melting point as 165°.

Anal. Calcd. for $C_8H_{12}O_6$: C, 47.07; H, 5.88. Found: C, 47.05; H, 5.9.

This acid, m. p. 167°, formed approximately 65% of the acid material. From the mother liquor a quantity of a sirupy acid was obtained, probably α,β-dimethyl-γ-carboxyglutaric acid.

Attempted Methylation of β,γ-Dimethyl-γ-carboxyglutaric Ester.--One and one-tenth grams of sodium was converted into anhydrous sodium ethoxide, and 12 g. of β,γ-dimethyl-γ-carboxyglutaric ester was added to the ether suspension cooled in ice. Although shaken for thirty minutes, not all the sodium ethoxide dissolved; 7.5 g. of methyl iodide was added and in a few minutes sodium iodide separated. The mixture was permitted to stand for six hours at room temperature. The material was then worked up in the usual way and the neutral products on distillation gave the following two main fractions: b. p. 80–100° (12 mm.), 8.0 g. of crotonic ester, dimethylmalonic ester; b. p. 160–162° (10 mm.), 3.5 g. of unchanged ester. Upon saponification, the last fraction gave entirely β,γ-dimethyl-γ-carboxyglutaric acid, m. p. 167°, showing that the only change that took place was the fission of the main part of the ester into crotonic and sodium enol methylmalonic esters.

Addition of **Methylmalonic** Ester to **Crotonic** Ester.—The methylmalonic ester used in the following experiments was prepared by methylation of sodium enol malonic ester and was purified from malonic ester by shaking out the latter with 25% caustic potash in the cold.[16]

(a) Using a Small Amount (One-Sixth Molecule) of Sodium Ethoxide.—0.75 g. of sodium was dissolved in 10 cc. of ethyl alcohol, 35 g. of methylmalonic ester was added, followed by 23 g. of crotonic ester and 300 cc. of dry ether. The whole was refluxed for five hours, then cooled and 2 g. of acetic acid in 20 cc. of water added. The ethereal solution was washed with 10% sodium carbonate. A yield of 49 g. of ester, b. p. 155" (2 mm.), was obtained. Saponification of this ester gave a mixture of acids which consisted of approximately 90% β,γ-dimethyl-γ-carboxyglutaric acid, m. p. 167°, together with 10% of α,β-dimethyl-γ-carboxyglutaric acid.

(b) Using One Molecular Equivalent of Sodium Ethoxide.—Four and six-tenths g. of sodium was converted into anhydrous sodium ethoxide; 35 g. of methylmalonic ester was added to the ethereal suspension, followed by 23 g. of crotonic ester and 300 cc. of ether. The mixture was refluxed for five hours, cooled, poured into 100 cc. of water containing 12 g. of acetic acid and worked up in the usual manner. On distillation 20 g. of unchanged esters, b. p. 60–100° (12 mm.), was first obtained, followed by 32 g. of ester, b. p. 148–150° (3 mm.), which proved to be α,β-dimethyl-γ-carboxyglutaric ester; yield, 60%.

Anal. Calcd. for $C_{14}H_{24}O_6$: C, 58.33; H, 8.33. Found: C, 58.25; H, 8.4.

α,β-Dimethyl-γ-carboxyglutaric acid was obtained by saponification of the above

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[15] Thorpe and Young, *J.* Chem. *Soc.*, 83, 358 (1903).

[16] Michael, *J. prakt. Chem.*, 72, 537 (1905).

ester with caustic soda. It was obtained as a sirup which in a desiccator became a solid. This was broken up, rubbed with chloroform and recrystallized from a mixture of ether and ligroin, m. p. 145°.

Anal. Calcd. for $C_8H_{12}O_6$: C, **47.07; H, 5.88.** Found: **C, 47.13; H, 5.99.**

This acid was identified as α,β-dimethyl-γ-carboxyglutaric acid by mixed melting point with the acid prepared from the condensation product of sodium **enol** malonic ester with **tiglic** ester.

Upon distillation of this acid, m. p. 145°, a mixture of ***cis*** and ***trans*** **α,β-dimethyl**glutaric acids was produced. This was separated by conversion of the ***cis*** acid into the anhydride and thence into the imide by treatment with dry ammonia **gas** at 130°. The ***trans*** acid was extracted with sodium carbonate from the reaction mixture, leaving the pure imide, m. p. **113'.** Hydrolysis of the imide with caustic soda gave the ***cis*** **α,β-dimethylglutaric** acid, m. p. 87°. The ***trans*** acid was a liquid.[17]

Similarly. distillation of **β,γ-dimethyl-γ-carboxyglutaric** acid, m. p. 167°, gave ***cis*** and ***trans*** a,@-dimethylglutaricacids, which were separated through the imide. These were shown to be identical with the ***cis*** and ***trans*** **α,β-dimethylglutaric** acids obtained from α,β-dimethyl-γ-carboxyglutaric acid.

Methylation of α,β-Dimethyl-γ-carboxyglutaric Ester.—One and two-tenths grams of sodium was converted into anhydrous sodium ethoxide and **14.5** g. of **α,β-dimethyl-γ-carboxyglutaric** ester was added to the ether suspension, cooled in ice water. The sodium ethoxide readily dissolved, **8 g.** of methyl iodide was added and the mixture left to stand for six hours. The product was then worked up in the usual way; **14** g. of α,β,γ-trimethyl-γ-carboxyglutaric ester, b. p. 164° **(3** mm.), was obtained.

Anal. **Calcd. for** $C_{15}H_{26}O_6$: C, 59.6; H, 8.61. Found: C, 59.4; H, 8.6.

α,β,γ-Trimethyl-α-carboxyglutaric acid was obtained from the above ester by saponification with caustic soda. The acid was obtained as a sirup which could not be crystallized.

Anal. Calcd. for $C_9H_{14}O_6$: **C, 49.53; H, 6.45.** Found: **C, 49.83;** H, **6.52.**

Upon distillation the acid gave the ***cis*** and ***trans*** forms of **α,β,γ-trimethylglutaric** acid.

Action of Sodium Ethoxide upon **β,γ-Dimethyl-γ-carboxyglutaric** Ester.—Fourteen and five-tenths grams of the ester was refluxed for six hours with an ethereal suspension of sodium ethoxide prepared from 1.2 g. of sodium by Briihl's method. After **cooling,** the product was poured into a solution of 4 g. of acetic acid in water, and the mixture worked up in the usual manner; 7 g. of the neutral ester boiling below 150° **(15** mm.) consisted of crotonic and methylmalonic esters; **6** g. of ester boiled at 160–163° (15 mm.). This ester was saponified and found to consist mainly of **α,β-dimethyl-γ-**carboxyglutaric acid, m. p. **145°.** A small amount **(0.5 g.)** of **β,γ-dimethyl-γ-carboxy-**glutaric acid, m. p. 167°, separated from this material was formed from unchanged ester.

Addition of Malonic Ester to Tiglic Ester.—Twelve grams of malonic ester was added to sodium ethoxide prepared by **Brühl's** method from **1.8** g. of sodium; 9 g. of **tiglic** ester, b. p. 158° **(760** mm.), was added and the ethereal solutiop heated on a **water-**bath for five hours. Working up the products in the usual manner gave a yield of 3 g. of α,β-dimethyl-γ-carboxyglutaric ester, b. p. 150° (3 mm.).

Anal. Calcd. for $C_{14}H_{24}O_6$: **C, 58.33; H, 8.33.** Found: **C, 58.1; H, 8.4.**

α,β-Dimethyl-γ-carboxyglutaric acid was obtained from the above ester by saponification with caustic soda. It crystallized in well-defined prisms, m. p. **145'** with decomposition.

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[17] Thorpe, J. Chem. *Soc.*, **83, 358 (1903).**

Anal. Calcd. for $C_8H_{12}O_6$: C, 47.07; H, 5.88. Found: C, 47.15; H, 5.8.

Larger quantities of this acid were prepared from the product of addition of sodium enol cyanacetic ester to tiglic ester.[18] The yield of α,β-dimethyl-γ-cyanoglutaric ester was 65% and it boiled at 143° (3 mm.). α,β-Dimethyl-γ-carboxyglutaric acid, obtained from the cyano ester by hydrolysis with caustic potash, was identical with the substance prepared by the other two methods.

α,β,γ-Trimethyl-γ-cyanoglutaric Ester.—Twelve grams of α,β-dimethyl-γ-cyanoglutaric ester was added to sodium ethoxide prepared from 1.2 g. of sodium and to the cooled ether solution 8 g. of methyl iodide was added, After standing for six hours. the mixture was worked up as usual. α,β,γ-Trimethyl-γ-cyanoglutaric ester distilled at 160° (2 mm.).

Anal. Calcd. for $C_{13}H_{21}O_4N$: C, 61.2; H, 8.24. Found: C, 60.9; H, 8.3.

α,β,γ-Trimethyl-γ-carboxyglutaric acid was obtained by hydrolysis of the above ester with a 20% caustic potash solution. The acid was obtained as a sirup.

Anal. Calcd. for $C_9H_{14}O_6$: C, 49.53; H, 6.45. Found: C, 49.6; H, 6.6.

F. E. Ray[19] prepared this acid from the ester obtained upon methylation of α,β-dimethyl-γ-cyanoglutaric ester, and described it as a solid. m. p. 144–145°. (It may be noted that 145° is the melting point of α,β-dimethyl-γ-carboxyglutaric acid.)

α,β,γ-Trimethylglutaric Acid.—α,β,γ-Trimethyl-γ-carboxyglutaric acid was heated at 160° in a distilling flask for thirty minutes, when the evolution of carbon dioxide ceased. The residue was then distilled, coming over at 170–180° (15 mm.) and partially solidifying in the receiver. This distillate was a mixture of *cis* and *trans* acids which were separated by the conversion of the *cis* form into the imide in the following way. The mixture, in a small distilling flask, was converted into the anhydride by several treatments with acetyl chloride. The acetic acid formed was removed under reduced pressure and dry ammonia gas passed through the sirupy mass at 130° for one hour. The cooled contents was dissolved in dilute hydrochloric acid. The acid solution was extracted with ether and the extract washed with aqueous sodium carbonate to remove the *trans* acid. Upon concentration of the ether solution the imide crystallized out.

α,β,γ-Trimethylglutarimide was recrystallized from a mixture of ether and ligroin, m. p. 90°.

Anal. Calcd. for $C_8H_{13}O_2N$: C, 61.94; H, 8.38. Found: C, 61.8; H, 8.2.

Cis-α,β,γ-trimethylglutaric acid was obtained from the α,β,γ-trimethylglutarimide by hydrolysis with 20% caustic soda. It crystallized from an ether and ligroin mixture in large prisms which, after the fourth crystallization, softened at 115° and melted at 125°.

Anal. Calcd. for $C_8H_{16}O_4$: C, 55.2; H, 8.06. Found: C, 55.6; H, 8.3.

Cis-α,β,γ-trimethylglutaric anhydride was a liquid. It was prepared from the above acid by treatment with acetyl chloride.

Trans-α,β,γ-trimethylglutaric acid was obtained by acidification of the sodium carbonate extract in the above separation from the *cis* imide. It remained a liquid and resisted all attempts to obtain a crystalline form.

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.2; H, 8.04. Found: C, 55.0; H, 8.2.

F. E. Ray[19] described an α,β,γ-trimethylglutaric acid melting at 134°. He did not attempt to separate his product into the *cis* and *trans* forms, but obtained his acid by a series of crystallizations.

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[18] Blaise, Bull. *soc. chim.*, [3]29, 332 (1903).

[19] Ray, This Journal, 50, 558 (1928).

β-Phenyl-γ-carboxyglutaric ester was prepared by addition of malonic ester to cinnamic ester using a small amount of sodium ethoxide; yield, 70%; b. p. 187° (4 mm.).[20]

β-Phenyl-γ-carboxyglutaric acid was obtained by saponification of the above ester with 10% caustic soda. This acid crystallizes from a mixture of chloroform and ligroin in fine needles, m. p. 137°.

Anal. Calcd. for $C_{12}H_{12}O_6$: C, 57.15; H, 4.76. Found: C, 56.9; H, 5.0.

Methylation of β-Phenyl-γ-carboxyglutaric Ester.—Thirty-four grams of the above ester was added to anhydrous sodium ethoxide prepared from 2.3 g. of sodium in ether; 15 g. of methyl iodide was added, the mixture allowed to stand in ice water for six hours, and the material worked up in the usual manner. On distillation of the neutral product, 17 g. boiled from 80–140° (3 mm.) and consisted of cinnamic and dimethylmalonic esters and 12 g. of γ-methyl-β-phenyl-γ-carboxyglutaric ester boiled at 194° (3 mm.).

And. Calcd. for $C_{19}H_{26}O_6$: C, 65.13; H, 7.43. Found: C, 65.0; H, 7.6.

γ-Methyl-β-phenyl-γ-carboxyglutaric acid was obtained from the above ester by saponification with caustic soda. On crystallization from a mixture of chloroform, acetone and ligroin, the acid first deposited fine needles which melted at 188° with decomposition.

And. Calcd. for $C_{13}H_{14}O_6$: C, 58.64; H, 5.26. Found: C, 58.4; H, 5.4.

The mother liquor then deposited a second acid crystallizing in large prisms, m. p., 148°.

Anal. Calcd. for $C_{13}H_{14}O_6$: C, 58.64; H, 5.26. Found: C, 58.3; H, 5.1.

These two acids are isomeric forms of γ-methyl-β-phenyl-γ-carboxyglutaric acid. The fine crystals of the acid, m. p. 148°, upon standing on a porous tile became converted into a form of m. p. 188° in the course of several hours. Large, well developed crystals of the low-melting form could be kept in a corked vessel for several months without change.

Carter and Lawrence[21] described γ-methyl-β-phenyl-γ-carboxyglutaric acid which they prepared by methylation of β-phenyl-γ-cyanoglutaric ester and saponification of the resulting γ-methyl-β-phenyl-γ-cyanoglutaric esters (which they obtained in two stereoisomeric forms) with caustic potash. They found that each of these stereoisomeric cyano esters gave the same γ-methyl-β-phenyl-γ-carboxyglutaric acid, m. p. 148'. Since they did not report obtaining any of the form of m. p. 188°, their synthesis was repeated. It was found that hydrolysis with alkali of each of the two **γ-methyl-β-phenyl-γ-cyanoglutaric** esters gave the acid of m. p. 148°, but this could be converted into the form of m. p. 188°.

Addition of Methylmalonic Ester to Cinnamic Ester

(a) Using a Small Amount of Sodium Ethoxide.—One-half gram of sodium was dissolved in the minimum of ethyl alcohol, 20 g. of methylmalonic ester added, then 200 cc. of dry ether and finally 20 g. of cinnamic ester. The mixture was refluxed on the water-bath for five hours, cooled and a solution of 2 g. of acetic acid in 20 cc. of water added. The product was worked up in the usual way; 16 g. of ester boiling at 80–140° (3 mm.) consisted of apparently unchanged esters; 20 g. boiling at 194–195° (3 mm.) proved to be **γ-methyl-β-phenyl-γ-carboxyglutaric** ester, since upon saponification it gave the corresponding acid.

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[20] **Michael,** *J. prakt.* Chem. 35, 350 (1887).

[21] Carter and Lawrence, *Proc. Chem. Soc.*, **178 (1900).**

(b) Using One Molecular Equivalent of Sodium Ethoxide.—Twenty grams of methylmalonic ester was added to a suspension of sodium ethoxide prepared from 2.6 g. of sodium in dry ether; 20 g. of cinnamic ester was added and the mixture refluxed on the water-bath for six hours. After cooling, 7 g. of acetic acid in 50 cc. of water was added, and the ethereal extract worked up in the usual way. The neutral esters were fractionated and 16 g., b. p. 185–188° (3 mm.), was obtained.

Anal. Calcd. for $C_{19}H_{26}O_6$: C, 65.13; H, 7.43. Found: C, 64.9; H, 7.51.

α-Methyl-β-phenyl-γ-carboxyglutaric acids were obtained from the above ester upon saponification with caustic soda, thus proving its structure. The acid first deposited from solution in a mixture of chloroform, acetone and ligroin had a melting point of 171°. The mother liquor deposited a second acid, which crystallized in fine needles, m. p. 145°. These two acids, present in approximately equal amounts, were shown by analysis and mixed melting point to be identical with the corresponding acids synthesized from α-methylcinnamic ester.

Addition of Sodium Enol Cyanacetic Ester to α-Methylcinnamic Ester.—Three and six-tenths grams of sodium was dissolved in 50 cc. of alcohol and 17 g. of cyanacetic ester added, followed by 29 g. of a-methylcinnamic ester. The mixture was heated on the water-bath for twenty-four hours. After cooling, the product was poured into a solution of 10 g. of acetic acid in 200 g. of water, and the esters were extracted with ether. On fractionation of the neutral esters, 26 g. of α-methyl-β-phenyl-γ-cyanoglutaric ester, b. p. 185–187° (3 mm.), was obtained as a thick liquid.

Anal. Calcd. for $C_{17}H_{21}O_4N$: C, 67.33; H, 6.93. Found: C, 67.15; H, 7.1.

α-Methyl-β-phenyl-γ-carboxyglutaric acids were obtained by hydrolysis of the above ester with caustic potash. Upon fractional crystallization, the first acid was deposited as large prisms, m. p. 171°, with decomposition.

Anal. Calcd. for $C_{13}H_{14}O_6$: C, 58.49; H, 5.26. Found: C, 58.49; H, 5.5.

From the mother liquor a second acid was deposited as fine needles, m. p. 145° with decomposition.

Anal. Calcd. for $C_{13}H_{14}O_6$: C, 58.49; H, 5.26. Found: C, 68.30; H, 6.4.

Summary

1. It has been shown that the course of addition of methylmalonic ester to crotonic and cinnamic esters varies with the amount of sodium ethoxide used.

2. In the presence of small amounts of sodium ethoxide the addition proceeds with H and $—C(CH_3)(COOEt)_2$ as addendum components.

3. In the presence of a molecular equivalent of sodium ethoxide the addition proceeds with CH_3 and $—C(COOEt)=C(ONa)OEt$ as addendum components.

4. These results have rigorously proved the correctness of Thorpe's conclusions: that the addition of sodium enol cyanacetic ester to a-methylacrylic ester takes place with migration of the hydrogen atom and that the addition of sodium enol a-cyano propionic ester to β,β-dimethylacrylic ester takes place with migration of the methyl group.

5. The mechanism of these reactions is discussed and explanations of the results are suggested.

Converse Memorial Laboratory
Cambridge, Massachusetts

NOTES

The Reduction of 1-Cystine to 1-Cysteine.—In a recent paper by Max Bergmann and Giorgios Michalis[1] a method is described for the catalytic hydrogenation of 1-cystine to 1-cysteine by means of "Palladium Mohr" and hydrogen. The authors also emphasized the possible importance of such a method for certain biological work in which metal-free cysteine preparations are desirable.[2] The use of dissolved metal salts for the reduction can be excluded with this method.

On the other hand Vincent du Vigneaud, L. F. Audrieth and H. S. Loring have presented a paper on "The Reduction of Cystine in Liquid Ammonia by Metallic Sodium" at the meeting of the Federation of the American Societies for Experimental Biology held at Chicago University on March 26, 1930. Without actually having heard this paper it is to be assumed from its title that it has anticipated the results obtained by the present author on the same subject, who also had found the system liquid ammonia–sodium to be a suitable reducing agent for 1-cystine. However, some sodium sulfide and alanine also were found to be formed in the course of the reaction.

Another reduction method for 1-cystine using aluminum amalgam as a reagent was simultaneously developed by the author and found to have some merits. This amalgam offers the possibility of reducing in aqueous solution, a minimum amount of dissolved metal salts being involved in the reaction due to the insolubility of the aluminum hydroxide formed. This and other advantages of the aluminum amalgam reduction process have been emphasized already several times before. An actual example was given in THIS JOURNAL in the reduction of phenylsulfonylchlorides to the corresponding mercaptans.[3]

A brief outline for the 1-cystine reduction, therefore, will be sufficient. 1-Cystine is dissolved in carbon dioxide-free water and 1–1.5 times its weight of aluminum amalgam[4] is added. The mixture is heated for approximately one hour. During this time the evolution of some hydrogen sulfide is noticed (hydrogen sulfide is also evolved in the course of the ordinary reduction using tin and hydrochloric acid; see Harrison, Ref. 2). The material is filtered with suction and washed with carbon dioxide-free water until the test with ferric chloride is negative. The filtrate and washings are combined, acidified with hydrochloric acid and evaporated to dryness in a vacuum at as low a temperature as possible. The crystalline

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[1] Bergmann and Michalis, *Ber.*, 63, *987* *(1930).*

[2] O. Warburg and S. Sakuma, Arch. *ges. Physiol* (*Pflügers*), 200, *203* *(192.7);* S. Sakuma, *Biochem.* Z., 142, *68* *(1923);* D. C. Harrison, Biochem. J., 18, *1009* *(1924).*

[3] E. Gebauer-Fuelnegg. *THIS* JOURNAL, 49, *1386* *(1927).*

[4] Prepared according to the procedure given by Wislicenus, *J. prakt. Chem.*, 54, *18* (1896).

residue consists mainly of l-cysteine hydrochloride, which can be separated readily from very small amounts of foreign matter by recrystallization,

CONTRIBUTION FROM THE
MEDICAL SCHOOL OF
NORTHWESTERN UNIVERSITY
CHICAGO, ILLINOIS
ERICA GEBAUER-FUELNEGG

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Chlor Phenol Red.—During the past summer this Laboratory had occasion to examine colorimetrically several commercial samples of this indicator from various sources. The wide variation in the color produced by the indicator in buffer solutions led to a careful examination of the samples.

Anal. Calcd. for dichlorophenolsulfonephthalein. $C_{19}H_{12}O_5SCl_2$: S, 7.58; Cl, 16.76. Found: Sample A, S, 6.76; Cl, 13.5; Sample B, S, 6.54; Cl, 16.00; Sample C, S, 7.14; Cl, 12.10; Sample D, S, 6.48; Cl, 8.46.

This indicator was first prepared by Cohen[1] by condensing *o*-chlorophenol with the crystalline anhydride of o-sulfobenzoic acid and subsequently crystallizing the crude product from glacial acetic acid.

The experience of this Laboratory has been that repeated crystallization from acetic acid will not give a pure product. By repeatedly dissolving the crude dye in hot water, acidifying with hydrochloric acid and concentrating on the water-bath to the point of crystallization, a product was obtained that gave the analysis: S, 7.60; Cl, 16.66.

This sample consisted of small, fine, greenish-brown crystals and gave an entirely different color in buffer solutions than samples heretofore examined. The alkaline color, besides being much more intense, contained more blue and less red than the commercial samples.

CHEMICAL RESEARCH LABORATORY
HYNSON, WESTCOTT & DUNNING, INC.
BALTIMORE, MARYLAND
WILTON C. HARDEN

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[1] U. S. Public *Health Reports*, 41, No. 53 (1926).

COMMUNICATIONS TO THE EDITOR

X-RAY INVESTIGATIONS ON RUBBER

Sir:

During some earlier x-ray investigations on crêpe rubber, it was observed that the originally translucent sample became more and more milky at the spot where the x-rays passed the material. The sample was the same as described in an earlier paper.[1] This rubber gave a distinct x-ray pattern during the first exposure, but, although the lines did not change their position, they became increasingly sharper with each exposure; simultaneously the opaqueness of the milky spot increased. The increase of sharpness of the originally broad lines represents, of course, increase in particle size; but evidently also the increasing cloudiness of the crepe rubber shows progressing crystallization

Another sample of the crepe rubber was placed in front of the window of the x-ray tube and again slowly the milky spot formed becoming eventually entirely opaque toward transmitted light. The spot obtained was sharply defined by the transmitted x-ray beam and showed no diffuseness at the circumference. After four years of storage, no further changes occurred in the sample. Upon slight warming the milky spot would melt away again.

An increase in the rate of crystallization of gutta-percha, but not of rubber, by means of ultraviolet light was observed by Kirchhof.[2]

Evidently the above sample of rubber behaves similarly under the influence of x-rays as does gutta-percha with ultraviolet light.

DEPARTMENT OF CHEMISTRY
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND
EMIL OTT

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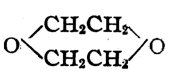
THE RAMAN SPECTRUM OF DIOXANE

Sir:

During the course of an investigation of the Raman spectrum of some synthetic resins, the solvent dioxane was used. As the spectrum of the latter has not been published previously, I wish to report here my findings.



Dioxane

An apparatus designed by Reynolds and Benford [*Review of Scientific* Instruments, 1, 413416 (1930)] was used, modified by having a chromium elliptical reflector instead of a silver one, and its major axis in a horizontal rather than a vertical plane. A mercury arc gave the exciting spectrum, exposures of about six hours being made.

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[1] E. Ott, *Naturwissenschaften,* 14, 320 (1926).

[2] Kirchhof, *Kautschuk,* 4,254 (1928); *C. A.*, **23**, 1525 (1929).

The reciprocals of the wave lengths of the modified lines were as follows (the intensities are given in parentheses) and are accurate probably to within 6 cm.$^{-1}$.

24426 (0), 225 (0), 23878 (4), 691 (3), 590 (1), 496 (1), 408 (2), 267 (2), 22507 (00), 422 (0), 099 (4), 21997 (00), 930 (1), 853 (3), 744 (5), 21640 (1), 556 (0), 501 (1), 20214 (00), 088 (4), 19972 (5). The lines were correlated, respectively, as follows, the ordinal numbers in the preceding list being given first, followed by the respective wave number shift.

Exciting line								Average $\Delta\bar{\nu}$
	24710		24522		22941		23047	
1	284 (0)	2	297 (0)	9?	434 (00)			291 (0) cm.$^{-1}$
3	838 (4)	4	831 (3)	10?	519 (0)			837 (4)
5	1120 (1)	7	1114 (2)	11	842 (4)	13	1117 (1)	1117 (1)
6	1214 (1)							1214 (1)
8	1443 (2)			18	1440 (1)			1442 (2)
12?	2713 (00)			19	2727 (00)			2720 (00)
14	2866 (3)	16	2882 (1)	20	2853 (4)			2864 (3)
15	2966 (5)	17	2966 (0)	21	2969 (5)			2967 (3)
								434 (00)?
								519 (0)?

Research Laboratory
General Electric Company
Schenectady, New York

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D. S. Villars

THE PHOTOCHEMICAL POLYMERIZATION OF ACETYLENE

Sir:

It has been reported by several observers[1] that the polymerization of acetylene to a solid resembling cuprene is induced by either activated mercury atoms or by the direct absorption of ultraviolet light. A quantitative investigation of the photochemical reaction has been undertaken in the hope of throwing some light on the kinetics of the process and to determine whether there is any simple relation between the ***quantum yield*** and ***the ion pair yield*** of the analogous radiochemical reaction.[2]

The following are some of the more important results of this investigation. Using the complete radiation of a quartz mercury arc and a reaction vessel three centimeters deep, the reaction velocity was observed to be proportional to the pressure of acetylene as long as this pressure was not greater than 30 cm.; at higher pressures the velocity approached a constant value. It seems probable therefore that the rate of polymerization

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[1] Berthelot and Gaudechon, *Compt. rend.*, *150*, 1169 (1910); Bates and Taylor, This Journal, 49, 2437 (1927); Reinike, *Z. angew. Chem.*, *41*, 1144 (1928).

[2] Lind, Bardwell and Perry, This Journal, 48, 1556–1575 (1926); Mund and Koch, *Bull. soc. chim. Belg.*, *34*, 241–255 (1926).

is proportional to the intensity of the absorbed light but is otherwise independent of the acetylene pressure. Using the same light source, the temperature coefficient of the reaction was determined by comparing the rate at 12 and at 39°. The ten degree temperature coefficient, so determined, has a value of 1.25. It is quite possible that this observed value may be largely the temperature coefficient of the light absorption rather than that of the chemical reaction. Experiments performed with light filters indicate that light of wave length 2537 Å. and longer is not efficient in producing the reaction; this is probably due to the comparative transparency of acetylene in this region.

Several determinations of the quantum yield have been made. The light source used in these experiments was a mercury arc combined with a focal isolation apparatus, which excluded all radiation of wave length greater than 2537 Å. A weighted average of $M/h\nu$, for three separate determinations, is 7.4 ± 2.5. The uncertainty of this value is due to the precipitation of cuprene on the walls of the reaction cell, which limited the measurements to the first two millimeters' reduction in pressure. These experiments will be repeated with a more sensitive manometer in order to obtain a more accurate value for the quantum yield. Similar experiments with allene and the homologs of acetylene are now in progress. In all experiments a "hot" mercury arc was used, pressures were measured with a quartz spiral manometer and liquid-air traps and gold foil were used to prevent the access of mercury vapor to the reaction system.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA

S. C. LIND
R. S. LIVINGSTON

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NEW BOOKS

Gmelins Handbuch der anorganischen Chemie. (Gmelin's Handbook of Inorganic Chemistry.) Edited by R. J. MEYER. Eighth edition. Beryllium. System-number 26. Issued by the Deutsche Chemische Gesellschaft, Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1930. xviii + 180 pp. 10 figs. 17 X 25 cm. Price, to subscribers, M. 23.50; singly, M. 30.

This volume covers the history of our knowledge of Beryllium, its occurrence, the preparation and properties of the free element and the preparation and properties of its compounds with elements having system-numbers smaller than 26, namely, the non-metals and the alkali metals. The literature has been covered to May 1, 1930.

The collaborators in the preparation of this volume were Martin Hosenfeld, Hellmut Fischer, Sibylle Cohn-Tolksdorf (atomic and optical properties) and Adrienne Eisner (the complex compounds).

This volume is yet another valuable addition to this useful reference work.

ARTHUR B. LAMB

Gmelins Handbuch der anorganischen Chemie. (Gmelin's Handbook of Inorganic Chemistry,) Edited by R. J. MEYER. Eighth edition. Cobalt. Part B. The Cobaltammines. System-number 58. Issued by the Deutsche Chemische Gesellschaft, Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1930. xxv + 376 pp. 2 figs. 17 X 25 cm. Price, to subscribers, M. 45; singly, M. 58.

The great group of the Cobaltammines whose broad outlines were first discerned by our own Wolcott Gibbs and F. A. Genth and which S. M. Jorgensen so greatly enriched, has been of much importance in the development of chemical theory—particularly as a basis for Alfred Werner's revolutionary and far-reaching ideas.

The first and indeed only adequate encyclopedia of our experimental knowledge of this group has been the volume entitled "Kobaltiake" written by Paul Pfeiffer and published as a part of the seventh edition of Gmelins Handbuch. The present volume is a revision and extension of this earlier work. Its original 290 pages have grown to 376 pages in spite of the use of finer type and the exercise of the greatest conciseness. The literature has been covered to the end of 1929.

Dr. Olga Angern (with Professor Pfeiffer's counsel), Dr. Mark von Stackelberg and Dr. Emma Haller collaborated in the writing and preparation of this book. It, like its predecessor, will be invaluable to anyone engaged in a study of this interesting group.

ARTHUR B. LAMB

Oxidation–Reduction Potentials. By L. MICHAELIS, Member of the Rockefeller Institute for Medical Research. Translated from the German Manuscript by Louis B. Flexner. J. B. Lippincott Company, East Washington Square, Philadelphia. Pennsylvania, 1930. xii + 199 pp. 16 illustrations. 14 X 21 cm. Price, $3.00.

During the past few years the author of this monograph has played an active part in the potentiometric study of those oxidation–reduction systems which are of particular interest to the biologist, and he has "thought it timely and useful to venture to weigh the investigations so far made, to collect and to analyze their application to biological problems and to discuss the theoretical principles of oxidation–reduction potentials with the hope that future work by others as well as by himself might be facilitated." An introductory discussion of the energy changes which may occur in living organisms is followed by an exposition of the more important aspects of the physical chemistry of inorganic and organic oxidation–reduction systems. The remainder of the book is devoted to a description of the physiological applications which have been made of these principles, with particular emphasis on the puzzling system formed by cystine and cysteine, to our knowledge of which Michaelis and his associates have generously contributed.

Those who have felt the need of some assistance in the problem of rapidly instructing the uninitiate in this modern field of research will not find their desires very well fulfilled by the new book, for it is addressed primarily to the expert rather than to the beginner The treatment throughout is critical, and the author's comments and historical notes, however interesting, do not always add to the clarity of presentation. The coining of the new word "redox" for "oxidation–reduction" and the inclusion in the text of the symbols "Rep," "Ret," "Oxp" and "Oxt" add neither to the beauty of scientific language nor to the simplification of the subject,

Those who are engaged in research on oxidation–reduction potentials will find in Michaelis' monograph an interesting commentary on those phases of the general subject which he has selected for discussion. Few will fail to find both matters which are treated quite to their liking and ideas with which they definitely disagree. Since little agreement among the critics themselves is to be expected, it is clear that Michaelis has hesitated neither to raise plenty of debatable questions nor to indicate his own opinion. Theoretical views, indeed, are often advanced with a considerable degree of enthusiasm. In the treatment of the long-standing question of the mechanism of oxidation–reduction, for example, Michaelis is well aware that equilibrium data, which represent the only facts yet available, furnish no clue to the mechanism, and yet he finds the hypothesis of electron exchange so attractive that he applies it even to the oxidation of basic substances in neutral or acid medium. It is necessary in this case to assume the *acidic* dissociation of a strongly basic group as a primary step in the oxidation. A less ardent supporter of the electron hypothesis would concede that the Wieland mechanism gives a more reasonable interpretation of this particular type of reaction.

While the newer ideas advanced by the author afford stimulating reading, one feels that they are to be regarded as suggestions rather than as well-rounded theories, for they do not always appear to be complete. Thus in developing a theory of the relation between color and oxidation potential the author states that the oxidized forms of the dyestuffs are without exception colored and the reduced forms colorless. He apparently has overlooked the striking relationship between the pale yellow anthraquinones and the intensely colored anthrahydroquinone ions.

In a field of work which is in the course of active development and which still presents numerous important problems, it is of value from time to time to have a comprehensive statement of the views of anyone whose work stamps him as an authority. Michaelis' monograph will be accepted as exactly fulfilling this function.

LOUIS F. FIESER

Diatomaceous Earth. By ROBERT CALVERT, Chief Chemist, Van Schaack Bros. Chemical Works, Chicago, Illinois. Book Department, The Chemical Catalog Co., Inc., 419 Fourth Avenue, at 29th Street, New Pork, U. S. A, 1930. American Chemical Society Monograph Series, No. 52. 251 pp. 15.5 X 23.5 cm.

The author of this American Chemical Society Monograph intends it as "a description of the present day industry of diatomaceous earth, an interpretation of the literature in the light of experience, and an indication of needed discoveries yet to be made in a new and interesting field of research."

He begins by explaining the structure and composition of diatomaceous earth with numerous photomicrographs showing the exquisite and varied forms of the diatoms whose fossilized remains have accumulated in enormous deposits in earlier geologic periods. The available statistics on production and trade throughout the world are assembled, showing that the amount mined in the United States exceeds the total in all the rest of the world by a substantial margin. The more important deposits are briefly described. The mining of the earth and its preparation for the market are discussed in considerable detail. The physical properties are expounded with special emphasis on the high porosity with the resultant low apparent density, great power to absorb liquids and low heat conductivity. Most of the book is devoted to present-day uses of the earth, the chief of these being for the filtration of sugar solutions, and for the manufacture of diatomaceous brick for thermal insulation, and as an addition to concrete. The **use** of diatotnaceous earth in these and in many other industries is discussed thoroughly. There is also a chapter on thermal conductance and loss of heat through furnace walls, which gives the theory and mathematics of conductance and insulation.

The book is well planned and clearly written, and offers a comprehensive review of the diatomaceous earth industry.

GRINNELL JONES
DOROTHY M. BOLLINGER

Organisch-chemisches Praktikum. **(Manual of Organic Chemistry.) By Dr.** LUDWIG **ORTHNER, Lecturer at the Technical High School of Karlsruhe, and Dr.** LUDWIG REICHEL, **Assistant at the Technical High School of Karlsruhe. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1929. xvi + 260 pp. 61 figs. 23.5 × 15.5 cm. Price, unbound, M. 9; bound, M. 10.**

This is an interesting, useful and well-written little handbook of organic preparations. The choice and spread of experiments is quite commendable. In keeping with the present trend of organic chemistry, there are a number of experiments dealing with natural products, with the synthesis of biologically important compounds, and with a few catalytic procedures. There are interspersed throughout the book, and particularly at the conclusion of each series of preparations dealing with a given type of compound, brief discussions of the fundamental chemistry of the series. That the authors have an appreciation of the physical chemistry viewpoint is also evident. The conventional chapter on analytical procedures differs uniquely from other texts of this character in that it describes the very useful and practical half-micro methods of H. ter Meulen and Heslinga. Taken as a whole, then, the book creates a decidedly favorable impression.

ARTHUR J. HILL

The Constitution of Sugars. By WALTER NORMAN HAWORTH, D.Sc., Ph.D., F.R.S., Professor of Chemistry and Director of the Department of Chemistry in the University of Birmingham. Longmans, Green and Company, 55 Fifth Avenue, New York City, 1929. vii + 100 pp. Illustrated. 15 × 24 cm. Price, $3.40.

This book gives a review of the more recent developments in the field of carbohydrate chemistry with which Professor Haworth's name is so closely linked.

The important part played by the ring configuration of sugars is being more and more recognized in biological, biochemical, physiological, botanical and industrial problems.

In the field relating to the structure of carbohydrates and polysaccharides, Professor Haworth's brilliant contributions are too well known to require note. Thanks to the masterly technique developed with the aid of his colleague, Dr. Hirst, assisted by a very able group of co-workers, it has been possible to establish the constitution of the majority of the sugars on a firm experimental basis and, while such views have not yet been accepted in their entirety in all quarters, it is, in the reviewer's opinion, merely a matter of a relatively short time before such will be the case.

The volume can be recommended most heartily to all students of carbohydrate and polysaccharide chemistry, as well as to all other students interested in obtaining a clear and accurate present-day picture of the structure of the products in this field.

HAROLD HIBBERT

Aluminiumchlorid in der organischen Chemie. (Aluminum Chloride in Organic Chemistry.) By GEORG KRÄNZLEIN, I. G. Farbenindustrie A.-G. Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1930. 47 pp. 15.5 X 2.35 cm. Price, M, 3.

The recent developments in the commercial production of aluminum chloride and the publicity given them make this booklet unusually timely. It presents a survey of the organic chemical uses of aluminum chloride in eleven subdivisions: the Friedel–Crafts reaction with its ramifications, the Fries rearrangement, the Scholl reaction, dehydrogenations, addition reactions, condensation reactions with the elimination of water, halogenations, nitrations, polymerization and condensation reactions, splittings and rearrangements, and the cracking of hydrocarbons. The technical and industrial values of the various reactions are emphasized. The book work is well done and the numerous formulas make for a clearer and more ready understanding of the complicated polynuclear compounds frequently introduced, The brochure is up-to-date, containing, as it does, citations from the literature of 1929. The large number of footnote references, 179 being given, include several to patents. This little volume will be of interest to anyone who is concerned with the scope of the use of a reagent, aluminum chloride, which promises to be of increasing significance in organic chemistry.

G. ALBERT HILL

Thyroxine. By EDWARD C. KENDALL, M.S., Ph.D., D.Sc., the Mayo Foundation, Rochester, Minnesota. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York 1929. 265 pp. 39 figs. **15 X 23.5 cm. Price, $5.50.**

The interested public—and it is a large one—owes much to Dr. Kendall's reserve in the preparation of this admirable monograph on this active agent of the thyroid gland. As the author notes in his preface, the book was one of the first to be announced in the series in which it appears, but actually it is the forty-seventh of the monographs to reach the public. The great interest in all that pertains to the thyroid both from the purely scientific and from the clinical viewpoints has led to a large amount of highly important investigative work during the last few years. By his well considered delay, Dr. Kendall has been able to give us a conspectus of these recent additions to knowledge in the field.

The author's own contributions are of the greatest significance, and the early chapters of the book are devoted to a summary of them, prefaced by a brief historical sketch. As a chemist, the author emphasizes that aspect of the work in these earlier chapters, giving a critical review of the methods adopted for the isolation of thyroxin, the proof of its constitution, and a summary of its physical and chemical properties. This naturally leads to a discussion of the iodine content of the thyroid gland, the only portion of the body known certainly to contain this demonstrably essential element in detectable amounts.

The author next turns to clinical consideration of the thyroid gland and its functional and organic derangements. Certain phases of mineral and nitrogen metabolism, the nervous influence of the secretory activity of the gland, Reid Hunt's acetonitrile test, and the effects of changed function on the respiratory and carbohydrate metabolism are successively considered.

It is well recognized that the thyroid is one of the potent regulators of growth and development, and chapters are allotted both to the results of spontaneous failure on various living forms and also to the stimulating effects of thyroid substances on the metamorphosis of amphibian larvae. Other chapters dealing with pharmacological studies include the standardization of thyroid preparations and their physiological activity; in addition, certain clinical and pathological material is discussed. With its well-known profound effect upon respiratory metabolism in the living organism, space is devoted to a consideration of possible mechanisms through which the active agent, thyroxin, may influence biological oxidations. The book concludes with a well selected bibliography listing five hundred and forty-one titles and well compiled author and subject indices. The book as a whole is a most excellent piece of work. While the author states that he has approached the task from the standpoint of a chemist, he has presented the clinical aspects in a way to be of interest and information to the practitioner. The selections from the over-abundant literature have been most judicious, and an adherence to factual evidence is maintained throughout, the latter a pleasing and refreshing contrast to some of even the more recent of the literature of the ductless glands. Dr. Kendall is to be congratulated on the production of a most readable and significant treatise on a subject of wide general interest and import.

A. W. ROWE

Essences naturelles et parfums. (Natural Essences and Perfumes.) By RAYMOND DELANGE, Chief, Services Scientifiques des Fabriques de Laire. Librairie Armand Colin, 103 Boulevard Saint-Michel, Paris, 1930. 222 pp. 11 × 17 cm. Price, unbound, 10.50 fr.; bound, 12 fr.

While this little handbook does not pretend to compete with the larger works on essential oils and perfumes, it should prove very valuable to those who wish to acquire a general knowledge of the chemistry of the subject.

A chapter on odor and its relation to the properties and molecular structure of substances is useful and interesting.

Chapters on analysis of oils and on the chemistry of the constituents of essential oils will be of interest to the worker in the laboratory.

The chapter on definite odoriferous compounds, both natural and synthetic, contains much valuable information.

The information given is accurate and concise.

The author states that by reason of the plan of the work he describes only a few of the more characteristic essential oils. Fifteen such oils are included, besides certain natural resins and some animal products used in perfumery.

The work includes a bibliography with references in the text.

E. K. NELSON

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COLLOIDAL PLATINUM AND ITS BEHAVIOR AS A TYPICAL ACIDOID SOL

BY S. W. PENNYCUICK

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For some time the author has been engaged on a series of investigations upon the structure, stability and general reactions of colloidal platinum.[1] The advancement of the work has reached a stage where it has proved desirable to present the collective evidence concerning the behavior of colloidal platinum as an acidoid sol, and to discuss the surface actions and the coagulation process, in the light of the more recent work.

Apart from its general interest as a negative hydrophobic sol, colloidal platinum presents added features of importance. Its catalytic powers are well-known and, further, the question arises as to whether each platinum particle in the presence of oxygen (or of hydrogen) does not behave as a tiny oxygen (or hydrogen) electrode. Investigations at present in hand lead to the hope that the results will ultimately throw light on catalytic actions and on electrode phenomena.

The Arcing of Platinum Poles.—All platinum sols used by the author were prepared by the Bredig method, using chemically pure platinum poles and conductivity water of specific conductivity less than 0.6×10^{-6}. The arcing was carried out in a closed vessel into which any required gas could be introduced. The negative pole showed the characteristic disintegration crater, and hence the platinum leaves this pole, probably with a negative charge. Some of the atomized platinum condenses on the positive pole, which accordingly becomes elongated. The rest is dispersed into the solution, but only a fraction of this remains suspended as the colloid. Although the solution is kept continually circulating and at a temperature close to 0°, the tips of the poles become red hot and the action there is violent. Conditions are, therefore, suitable for the reaction of the atomized platinum with the water or with the oxygen due to the electrolytic decomposition of the water. In any case, Rocasolano[2] has found

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[1] See *Australian* **J.** *Exp. Biol. Med. Science,* 4, 99 (1927); *J. Chem. Soc.,* 2600 (1927); 551, 2108 (1928); 618, 623 (1929); *Kolloid-Z.,* 49, 407 (1929).

[2] Rocasolano, "Colloid Chemistry (Alexander)," Vol. I, 1926, p. 678.

that only hydrogen gas is actually given off, and therefore the equivalent amount of oxygen has been taken up by the platinum. As finely divided platinum is relatively easily oxidized,[3] one may conclude that under the conditions cited the oxygen has been taken up to form definite oxidation products, such as oxides and oxy-acids.

The dissolved oxygen does not play a controlling part in the formation of these oxidation products, for if the preparation be carried out in the presence of nitrogen and the complete absence of oxygen[4] (or of air), a comparable sol is obtained. It is acidoid, it contains the same free strong platinic acid, but it is somewhat less stable (more readily coagulated on boiling) than the corresponding sol prepared in the presence of oxygen. Such sols will be referred to as platinum–nitrogen and platinum-oxygen sols, respectively. It will be convenient to point out here that the results obtained show that whilst the surface of the particles of the platinum–nitrogen sol contains some unoxidized platinum, the surface of the platinum–oxygen (or platinum–air) sol is wholly oxidized. If a stream of oxygen is passed into the former sol, sometime after preparation, its behavior is now comparable in every detail, with that of the platinum–oxygen sol. From these results one can assign the part played by the dissolved oxygen in the preparation of the latter sols.

The Free Electrolyte Produced by Arcing.—On dispersing from 100 to 150 mg. of platinum in a liter of water, the specific conductivity is of the order 6 to 8 X 10^{-6}, and this may be increased to 30 X 10^{-6} (or more) by boiling. From the weight of platinum present, and from the approximate radius of the particles (30 X 10^{-7} cm.), one may calculate that the molality of the dispersed platinum is of the order 10^{-10} M, and the specific conductivity due to the particles of the order 5×10^{-12}. This is, of course, immeasurably small. Now the total negative charge on the platinum is equal to the positive charge on the contra ions ("gegenionen"), and these as will be shown are hydrogen ions. In order that the conductivity of these ions should approach the average error shown in conductivity measurements (0.3 X 10^{-6}, corresponding to 0.000001 equivalent of hydrogen ion), it can be shown that each platinum particle must give rise to at least 10,000 "free" hydrogen ions. (By "free ions" are understood those which contribute the whole of their conductivity to the solution.) The evidence available leads us to believe that in no case does the number of free contra ions ever approach this value, and hence the conductivity of both the platinum particles and their hydrogen contra ions may be neglected. This conclusion is confirmed by the following experiment. When an acid such as hydrochloric or nitric is added to a pure platinum

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[3] Wohler, *Z. anorg. Chem.*, 29, 1 (1901); 40, 423 (1904).

[4] The oxygen due to the electrolytic decomposition of the water cannot, of course, be excluded.

sol and to a strictly comparable sample of the intermicellar fluid, the conductivity-concentration curves exactly coincide, even when carried right past the coagulation point. Hence the removal of the platinum with its hydrogen ion partners causes no alteration in the conductivity. The whole of the measurable conductivity of a platinum sol may, therefore, be attributed to the free electrolyte produced during the arcing process. The intermicellar fluid (referred to above) can be isolated so as to retain this electrolyte by freezing and then thawing the sol. This treatment completely coagulates the platinum and leaves the clear intermicellar fluid.

Although the amount of dissolved electrolyte is too small for exact quantitative identification, titration with bases shows that it is a strong acid. From a knowledge of the oxidation products of platinum, the author concludes that this free strong acid is hexahydroxyplatinic acid ($H_2Pt(OH)_6$), or one of its dehydration products, *e. g.*, $H_2PtO(OH)_4$. The amount present is always small, and an average sol of specific conductivity 15×10^{-6} contains 0.00004 equivalent. It will be shown later that many acids, including the common inorganic acids, coagulate at a constant hydrogen-ion concentration, namely 0.0002 N. It therefore appears that this would also serve as an approximate limiting maximum for the concentration of the hexahydroxy acid, in the preparation of stable sols.

If platinum sols are filtered in order to remove the larger particles or the products of coagulation, the free acidity may become completely destroyed by the filter paper. The work of Kolthoff,[5] Rona and Michaelis,[6] and Mokruschin and Kryloff[7] on the action of filter paper on acids, shows either that the acid is "adsorbed," or that there is an interchange of cations. To retain an acidoid sol in the absolutely pure state, filtering must be avoided, and any flocculated products removed by centrifuging or simply allowing the sol to stand for some time.

Hexahydroxyplatinic Acid as the Stabilizing Ionogen at the Colloid Surface.—In the theory of colloid structure as developed by Duclaux,[8] Gouy,[9] Debye and Hückel,[10] McBain,[11] Bjerrum,[12] Pauli and Engel,[13] Pauli and Schmidt,[14] and others, the colloid particles are regarded as huge multivalent ions which owe their charges to the ionization of surface ion-

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[5] Kolthoff, *Pharm. Weekblad.*, 57, 1571 (1920).

[6] Rona and Michaelis, *Biochem.* Z., 103, 19 (1920).

[7] Mokruschin and Kryloff, *Kolloid-Z.*, 37, 145 (1925); 43, 387 (1927).

[8] Duclaux, *J. chim. phys.*, 5, 29 (1907).

[9] Gouy, *J. phys.*, [4] 9, 457 (1910).

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

[11] McBain, *J. Phys. Chem.*, 28, 706 (1924).

[12] Bjerrum, *Z. physik. Chem.*, 110, 656 (1924).

[13] Pauli and Engel, *ibid.*, 126, 247 (1927).

[14] Pauli and Schmidt, *ibid.*, 129, 199 (1927).

ogens. In many cases the surface ionogen has been identified.[15] With colloidal platinum, the following considerations leave no doubt that the active ionogen is the strong platinic acid, which has already been identified as $H_2Pt(OH)_6$[16] or one of its near relations.

(a) First there is the general evidence that colloidal platinum prepared in conductivity water forms a stable sol. The surface ionogen necessary for stability must therefore have been formed during the arcing process. This immediately suggests that the ionogen is identical with the free acid present in the sol, and that probably an equilibrium exists between the amount combined and the amount free.

(b) On aging or on boiling, the conductivity steadily increases. The statement[17] that "many metallic sols, *e. g.*, colloidal platinum, coagulate quickly upon warming," is not correct. Pure platinum sols when prepared as above, can be boiled for hours. The increase in conductivity is due to the liberation (or formation) of more free electrolyte. On freezing out the platinum from the boiled sols, it can be shown, by titration with bases, that the whole of the electrolyte present (including that newly formed) is the strong platinic acid. As there is a possibility that boiling may favor the production of further acid by oxidation, the boiling has also been carried out in the absence of oxygen and in the presence of nitrogen. Similar increases in conductivity were always obtained; hence it may be concluded that the colloid particles contain some platinic acid, which is gradually liberated on boiling or on aging.

(c) On the addition of neutral salts it can be shown that the increase in acidity up to (and past) the coagulation point, is due to the ionic exchange of hydrogen contra ions for cations of the added salt. This result, together with the foregoing, offers conclusive evidence that the contra ions are hydrogen ions, the surface ionogen is an acid and the sol is an acidoid.

(d) In the presence of added acid, experiments show that the decrease in the cataphoretic velocity (or in the ζ-potential) is a linear function of the square root of the acid concentration. In terms of the Debye–Hückel theory as applied to colloids,[10] this result directly indicates that the added acid simply depresses the ionization of the surface acid until the critical potential is reached and coagulation ensues. This, in conjunction with the fact that acids coagulate at a fixed P_H, affords further direct evidence that the platinum sol is acidoid.

The Amount of Surface Acid.—It has proved extremely difficult to obtain an approximate idea of the fraction of surface covered by the acid. Quantitative examination of the platinum particles is of little use,

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[15] See Pauli and Valkó, "Elektrochemie der Kolloide," Wien, 1929, p. 95.

[16] Pennycuick *J. Chem. Soc.*, 2108 (1928).

[17] Freundlich, "Colloid and Capillary Chemistry," English Ed., 1926, p. 457.

for apart from the surface acid there appears to be a considerable amount of acid in the interior of the particle. Experiments with barium hydroxide indicate that a maximum of 25% of the surface is the hexahydroxy acid, but later work with other bases shows that this is far too high even as a guiding maximum. By calculating the amount of hydrogen ion displaced from the surface by barium ion in the presence of excess barium chloride, one obtains a maximum of 14% of surface acid. As in such cases hydrolytic cleavage is superimposed on the ionic replacement, the actual fraction is probably considerably less than this. Furthermore, the results indicate that in the pure sol an intimate relationship exists between the charge carried and the concentration of free hexahydroxy acid. A comparison of the free acid concentration and the ζ-potential, for a variety of pure sols, gave such irregular results as to suggest that the hexahydroxy acid is bound at the colloid surface only at active points, and that the latter vary with the age and the treatment of the sol. The percentage of surface acid, therefore, varies from sol to sol, and at present no reliable value can be given in any one case.

How is the Acid Held at the Surface?—There is nothing to be gained by laboring the different points of view as to whether the hexahydroxy acid is adsorbed or chemically combined at the surface. It must be pointed out, however, that explanations of surface action (adsorption) in terms of the single physical factor, surface energy, have proved notoriously infertile and incomplete. Ellis[18] and Powis[19] have demonstrated, in the case of oil emulsions, that the supposed intimate relation between adsorption, surface tension and electric charge, does not exist at all, whilst coagulation phenomena observed with oil drops, vanadium pentoxide and also with colloidal platinum, can be shown to have no connection with changes in interfacial tension. Furthermore, Laing, McBain and Harrison[20] have obtained results which appear to be quite contrary to the predictions of the Gibbs theorem.

The more useful interpretation that surface reactions take place through oriented and polar groups is to be preferred. Adsorption forces are then identified as those which produce chemical combination, any differences being only in degree. This is the point of view adopted by the writer, who considers that the anion of the hexahydroxy acid exists at the surface as part of the micelle structure, and the following evidence indicates that it is there combined with certain active molecules which are probably oxides. It has been pointed out that a platinum–nitrogen sol contains less surface oxide than a platinum–oxygen sol. The former is, moreover, less

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[18] Ellis, *Z. physik. Chem.*, 80, 597 (1912).

[19] Powis, *ibid.*, 89, 186 (1915).

[20] "Colloid Symposium Monograph," Chemical Catalog Co., Inc., New York, 1928, p. 631.

stable against boiling. If, however, it receives a stream of oxygen, its stability is now comparable with the platinum–oxygen sol. The stabilizing acid is therefore more strongly held, the more the surface is oxidized. Further, if hydrogen is passed into any sol, one would expect the surface oxides to be reduced, and in keeping, the sol immediately loses its acidoid properties; if oxygen is now re-introduced the acidoid properties are recovered. One therefore concludes that the hexahydroxy acid is only combined when there are surface oxides present.

The Nature of the Rest of the Surface.—As colloid reactions are fundamentally surface reactions, a knowledge of the nature of the surface is of primary importance. It has been shown that the hexahydroxyplatinic acid appears to be combined at the surface with oxides of platinum, and the evidence will now be briefly summarized which indicates that the rest of the surface is also some form of oxidized platinum.

Platinum sols can take up large amount of bivalent bases. Measurements show that these amounts are not only more than sufficient to neutralize the surface acid, but that they are approximately sufficient to cover the whole of the colloid surface with a unimolecular layer. If a stream of hydrogen is passed for a limited period into a pure sol, two results become evident, first, the acidoid properties immediately disappear, and, second, the sol cannot now take up any barium hydroxide at all. Under the action of the hydrogen the surface properties have thus become completely altered.[21] If a stream of oxygen be now passed, both the acidoid properties and the power of removing bases are restored, although both are somewhat weakened. The obvious explanation of these phenomena is that the particles of colloidal platinum, when in the presence of oxygen (or of air), are coated with some form of oxidized platinum which confers upon them their characteristic properties. The addition of hydrogen immediately reduces the surface oxides and hence destroys these properties. (The hydrogen also probably reduces some of the free hexahydroxy acid, but this action is relatively slow and is not allowed to become complete.) In keeping with the above it is found that a sol prepared and handled in the presence of nitrogen takes up less base than a normal sol, *i. e.*, one prepared in the presence of air. If, however, a stream of oxygen is passed into the former sol its power of removing bases is considerably increased. It therefore appears that the surface of the platinum–nitrogen sol contains some unoxidized platinum, which is turned into the oxide simply by passing oxygen.

The question might be raised as to whether the oxygen held at the surface is merely physically adsorbed and not chemically combined. This is really of secondary importance, the major point being that it is the surface

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[21] The sols containing hydrogen, although no longer acidoid, are quite stable in the absence of air. Such sols are at present under investigation.

oxygen which confers the normal properties on colloidal platinum. However, the indications are that definite compounds are formed. Freundlich[22] quotes general evidence that "oxygen appears to be bound by platinum in the true chemical sense," *e.* g., platinum containing oxygen dissolves in acid in proportion to its oxygen content; the temperature coefficient of the fixation is positive, and oxygen cannot be pumped off at ordinary temperatures. These observations were made with platinum metal, and as it is well known that substances in a finely divided state, particularly when newly formed, are more reactive than when in the coarse state, the same general conclusions doubtless hold for the colloidal metal. In fact the author has shown that colloidal platinum particles, in the presence of air, take up 20 to 30 times as much barium hydroxide as an equal area of platinum gauze or foil. As it has been shown that bases are only taken up by the surface in the presence of oxygen, we must conclude that the colloid surface is far more reactive toward oxygen than the metal surface. Again the fact that ordinary platinum sols, when placed in a reflux condenser and in a stream of nitrogen, can be boiled for hours, is further evidence that the surface oxygen is particularly strongly held.

Reactions at the Surface of Colloidal Platinum.—The simplest formula for a platinum sol would be of the nature

$$[x\mathrm{Pt}\cdot y\mathrm{PtO_2}\cdot z\mathrm{Pt(OH)_6}]^{2z-}\ldots\ldots 2z\mathrm{H}^+$$

Here the Pt represents, very incompletely, the constitution of the interior of the particle, PtO_2 conveniently represents the surface oxide, and $H_2Pt(OH)_6$ the surface ionogen. From all points of view the formula is incomplete, but the representation of the surface is sufficiently accurate to serve as a basis for the discussion of surface reactions. In keeping with the Debye–Hückel theory of the colloid as a strong electrolyte,[10] the surface ionogen is shown as completely ionized. One might compare this formula, especially with regard to surface structure, with that proposed by Pauli[23] for silicic acid sols, namely

$$[x\mathrm{SiO_2} + n\mathrm{H_2O}\cdot y\mathrm{SiO_3H}]^{y-} + y\mathrm{H}^+$$

Reactions at the surface fall into three distinct classes, and these will be discussed separately.

First, there is the ionic replacement of the hydrogen contra ions by the cations of added electrolyte. Although the $H_2Pt(OH)_6$ in the above formula is represented as wholly ionized, the hydrogen ions form an ionic atmosphere around each particle, and only a small fraction can be regarded as actually "free." On the addition of any salt, *e.* g., barium chloride, some of the barium ions enter the ionic atmosphere, displacing the equivalent amount of "bound" hydrogen ion. This is the fundamental action leading up to coagulation and, in keeping, both the replacement and the coagula-

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[22] Freundlich, Ref. 17, p. 153.

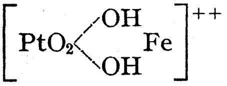
[23] See Pauli and Valkó, Ref. 15, p. 509.

tion depend upon the concentration, the valence and the specific properties of the cations concerned. This will be discussed in the section on "Coagulation;" it is sufficient to say here that in the case of colloidal platinum ionic replacement has been demonstrated with all types of salts.

Second, the surface oxide is an acidic oxide, and by combination with such added electrolytes as bases, etc., it may form either simple or complex salts. These-act as fresh surface ionogens, and cause an increase in the charge, greater stability and so on. These conclusions are based on considerable experimental evidence; for example, it may be shown with sodium hydroxide that a definite amount of base is removed by the colloid, and at the same time cataphoretic velocity of the particle, and the ζ-potential, are increased by more than 100 per cent. The combination of the base at the surface has thus produced fresh surface ionogens, and these are interpreted in the nature of salts. All bases act in a similar manner. Further, it may be shown that some few electrolytes, *e.* g., HCN, $K_4Fe(CN)_6$ and $K_2Pt(CN)_6$ are also removed by the colloid and at the same time cause an increase in the ζ-potential of the colloid particles, and hence a production of fresh surface ionogens. This reaction is interpreted as due to the formation of complex salts between the surface oxide and the added electrolyte, *e.* g., $[PtO_2\ldots CN]^- + H^+$, or $[PtO_2\ldots(CN)_6Pt]^= + 2K^+$. In keeping with the acid nature of the surface oxide, it is always a complex anion (never cation) which is formed, and this being bound at the surface increases the negative charge of the colloid. This also serves to explain the combination of the hexahydroxy acid itself at the surface, for as has already been pointed out this acid is bound only so long as there are platinum oxidation products there.

Third, we have the possibility of hydrolytic cleavage. One of the striking features of colloidal platinum is its great affinity for bases. As this is due to the acid nature of the surface, it follows that on the addition of a salt the ordinary partition effects would hold and the surface would claim its share of the base. Salts of weak acids, such as potassium acetate, contain a certain amount of free base by hydrolysis, and the results show that the platinum surface takes its share of this. Recent work, which will be published in detail elsewhere, shows that even with neutral salts the platinum surface takes a small but important fraction of base from the salt, leaving free acid behind.

The whole of the work carried out with colloidal platinum has not revealed the necessity for any further classification of surface reactions. All the so-called "adsorption" phenomena come under one of the above three headings. It is advisable to make this quite clear. It is generally accepted that adsorption compounds are Werner compounds, or at all events that they are essentially chemical at basis. Moreover, in the case of electrolytes (and electrolytes only are considered in this paper) the adsorption is polar. If the anion be oriented in toward the surface, the most probable and the most useful interpretation is the formation of a complex anion as described in the second case above. Now, the surface is essentially acidic, and whilst the formation of complex anions with the surface acid oxide (*e.* g., $[\mathrm{PtO_2}\ldots\mathrm{CN}]^- + \mathrm{K}^+$) is exceedingly probable, combination of the acidic oxide with cations (*e.* g., $[\mathrm{PtO_2}\ldots\mathrm{K}]^+ + \mathrm{CN}^-$) is exceedingly improbable. In keeping with this conclusion there is no experimental evidence that the distinctly acidoid sol, colloidal platinum, ever combines with a cation. Whenever cations are removed from solution and found at the surface, the action can always be traced either to ionic replacement or, to a lesser extent, to hydrolytic cleavage.

The reversal of sign experienced by colloidal platinum when ferric chloride or aluminum chloride is added, is generally interpreted as due to the adsorption of the cation at the surface. This explanation is not in keeping with the conclusions above, and in a paper which will appear shortly it will be shown that experiments with colloidal platinum demonstrate that the cation is not the reversing agent. Reversal is due to the reaction at the surface of the initial products of hydrolysis, probably the basic chloride, and the surface compound formed is of the nature  $\left[\mathrm{PtO_2}\genfrac{}{}{0pt}{}{\diagup\mathrm{OH}\diagdown}{\diagdown\mathrm{OH}\diagup}\mathrm{Fe}\right]^{++} + 2\mathrm{Cl}^-$. When excess of this is formed, the sol changes sign and becomes positive.

Coagulation

(a) Coagulation by Acids.—With acids such as hydrochloric, nitric, sulfuric and acetic, the evidence shows that there are no surface reactions beyond the attenuation of the hydrogen ionic atmosphere, due to the increase in the hydrogen-ion concentration of the solution. This is based largely upon three facts, (a) none of the added acid is taken up by the colloid, (b) the decrease in the ζ-potential is proportional to the square root of the acid concentration, and (c) acids coagulate at a fixed P_{H}.[24] With acids which react at the surface, e. g., hydrocyanic, the production of fresh ionogens exercises a stabilizing action which is opposed to the depression of the ionization due to the increase in the hydrogen-ion concentration of the solution. Such acids show a maximum in the ζ-concentration curve, and coagulate at a higher acidity depending on the extent of the surface action.

(b) Coagulation by Bases.—With univalent bases, *e. g.*, sodium hydroxide, the outstanding features are the rapid increase in the ζ-potential to a maximum, and the high coagulation concentration. These are obviously related and are due to the base reacting with the surface oxide to form fresh ionogens. The whole of the contra ions are univalent sodium

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[24] See *J. Chem. Soc.*, 551 (1928).

ions, and the increased charge on the particles necessitates an abnormal increase in the sodium-ion concentration to produce coagulation (compare coagulation concentrations, NaOH = 0.02 *N*, NaCl = 0.003 *N*).

Bivalent bases, e. g., barium hydroxide, show some characteristic differences The amount of base removed is four to five times greater than in the case of univalent bases, the increase in the ζ-potential is very much less, whilst the coagulating concentration is very low. These differences are brought out in Fig. 1. It may be assumed that the barium hydroxide reacts at the surface in the same way as the sodium hydroxide, namely, to form surface salts of the nature $[PtO_2\ldots O]Ba$, but the very small increase in the ζ-potential, and likewise the low coagulation concentration of the barium ion, show that the surface ionization is relatively small. The well-known fact that the concentration of the coagulating ion decreases very rapidly with valence is beyond doubt intimately connected with the interionic attractive forces between the colloid ion and the coagulating contra ions. When the valence of the latter is high, the ionic atmosphere is more confined or attenuated, the colloid charge is low and the sol is less stable. Accordingly small increases in the concentration of the free higher-valenced cations are sufficient to depress the ζ-potential to the critical value.

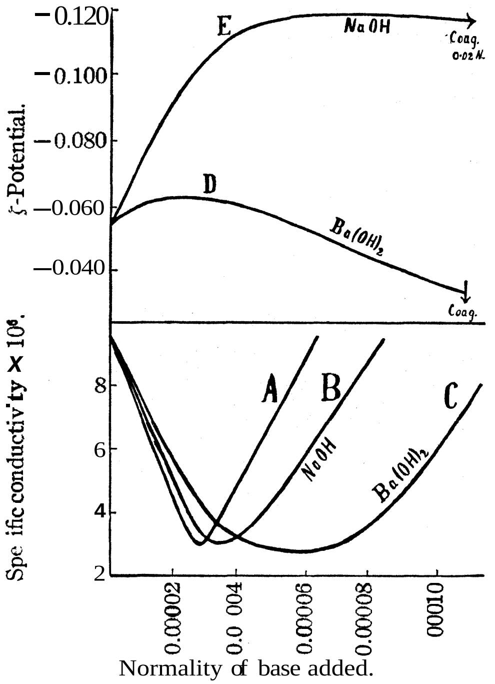

Fig. 1.—Curve A is the titration curve of the intermicellar fluid with NaOH and with $Ba(OH)_2$. Curve B is the titration curve of the platinum sol with NaOH. Curve C is the titration curve of the platinum sol with $Ba(OH)_2$. Curves D and E are the ζ-concentration curves for $Ba(OH)_2$ and NaOH, respectively (ζ-potential = cataphoretic velocity × 187.1).

(c) Coagulation by Salts.—On the addition of a salt, the first step, and the one which ultimately leads to coagulation, is the ionic replacement of the hydrogen contra ions by the cation of the added salt. This has been well illustrated in the case of barium chloride, as the following experiment shows. From a comparison of the curves obtained by following the conductivity changes on the addition of barium chloride to a platinum sol, and also to the intermicellar fluid, one may calculate the amount of hydrogen ion set free by exchange at any concentration of salt. With a sample of the same sol one may also follow the decrease in the ζ-potential for progressive additions of the same salt. By choosing convenient scales and plotting these changes on the one figure, it is found that the curves coincide (Fig. 2). Hence the changes due to ionic replacement agree step by step with those in the ζ-potential, It would thus appear that in such cases, the replacement of the hydrogen ion is the primary cause of the decrease in the ζ-potential and therefore in the stability of the colloid.

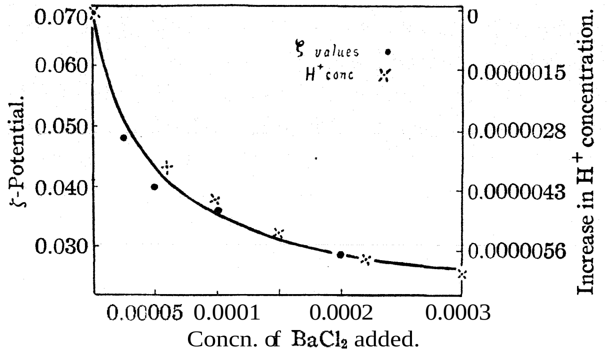

Fig. 2.

For many years it has been the practice to explain the coagulation of negative sols in terms of the "adsorption of the oppositely charged ion." It would now appear that for every oppositely charged ion "adsorbed," a surface contra ion is set free.[25] Hence the explanation in terms of the "adsorption of the oppositely charged ion"—an explanation which has been subject to rather loose usage—may be considered as having served its purpose. It should now be discarded and replaced by the more definite idea of ionic replacement.

Besides the usual replacement, some salts show appreciable formation of surface compounds or exhibit hydrolytic cleavage. The foregoing generalization may be extended to meet these cases. For example, with potassium cyanide, not only does the cyanide ion combine at the surface to form fresh ionogens but the potassium hydroxide of hydrolysis does likewise. Moreover, the extent of the combination increases with the concentration of potassium cyanide. Experiment shows that at low concentration this stabilizing action predominates and the charge increases, but at high concentration these are outweighed by the depression

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[25] See also Linder and Picton, J. *Chem. Soc.*, *61*, 114 (1892); Whitney and Ober, *Z. physik. Chem.*, *39*, 630 (1902); Pauli and Matula, *Kolloid-Z.*, 21, 49 (1917); Michaelis and Rona, *Biochem. Z.*, 97, 57 (1919); Pauli and Schmidt, *Z. physik. Chem.*, 126, 247 (1927); Rabinowitsch and Dorfmann. *ibid.*, 131, 313 (1928); Ganguli, *Phil.* Mag., [VII] 7,317 (1929).

of ionization due to the increase in concentration of the free potassium ions and this ultimately leads to coagulation.

The effect upon coagulation of changing the PH of an acidoid sol may now be generalized. If the sol be made more acid the colloid charge is depressed, and salt coagulation occurs at a lower concentration, whilst if the sol be made basic, fresh ionogens are formed and more salt is required to bring the ζ-potential to the critical coagulation value.

Action of Hydrocyanic Acid on Platinum Sols.—Hydrocyanic acid has an extremely important poisoning action on colloidal platinum, and although the investigations in this direction are incomplete, the results so far obtained may be presented here.

Experiments have been carried out to determine the effect on the cataphoretic velocity of increasing additions of hydrocyanic acid. For the purpose the Landsteiner–Pauli apparatus was used, with the intermicellar fluid as the overlying liquid. From the cataphoretic velocity, the ζ-potential is calculated by the usual formula.[26] The results are set out in Table I and shown by Curve A in Fig. 3. In contradistinction to the normal depression shown by hydrochloric and nitric acids, we find with hydrocyanic acid that there is an initial increase in the velocity of the particles, and a maximum at a concentration of approximately 0.0002 N. From the course of the curve it may be concluded that at low concentrations of hydrocyanic acid, the production of fresh surface ionogens and the consequent increase in charge predominate, whilst at higher concentrations the effect due to the depression of the surface ionization is the greater. We thus not only have a direct indication of the removal of hydrocyanic acid by the colloid surface, but we also have the interesting fact that the "poisoned" particle carries a bigger charge than normal. Now in the catalysis of hydrogen peroxide it is well known[27] that sodium hydroxide greatly increases the catalytic velocity, whilst the author has shown (see Fig. 1) that the same base causes an abnormal increase in the colloid charge. Other results agree in pointing to a relationship between the velocity of decomposition and charge carried. The nature of the interrelation is unknown, but the fact that hydrocyanic acid increases the charge

TABLE I

CHANGE IN THE ζ-POTENTIAL ON THE ADDITION OF HYDROCYANIC ACID ($\zeta = 6\pi\eta u/DH$). TEMPERATURE, 18°

Concn. of HCN	$u \times 10^5$	ζ
.....	-33.5	-0.063
0.000101	-40.0	- .075
.00024	-40.4	- .076
.00050	-33.8	- .063

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[26] Debye and Hückel, *Physik. Z.*, 25, 49 (1924).

[27] See discussion and references, Freundlich, Ref. 17, p. 489.

and at the same time poisons the catalyst, appears to the author to afford direct confirmation of the view that the poisoning is due to the combination of the hydrocyanic acid with catalytically active centers at the colloid surface.

Previous work with colloidal platinum has failed to give any information as to the amount of hydrocyanic acid combined with the surface. As the conductivity method has been used successfully by the author to measure small amounts of surface change, *e. g.*, ionic replacement, this sensitive method was applied to follow the changes in the platinum sol on the addition of hydrocyanic acid. For the purpose, samples of the very pure platinum sol and of the intermicellar fluid of exactly the same conductivity were placed in conductivity cells having suitable cell constants. Increasing amounts of hydrocyanic acid were added and the conductivity changes followed. The results are shown in Table II and by Curve B in Fig. 3. Bearing in mind that similar pairs of curves for hydrochloric and nitric acids showed exact correspondence, it was expected that the platinum sol curve, owing to the removal of hydrocyanic acid would

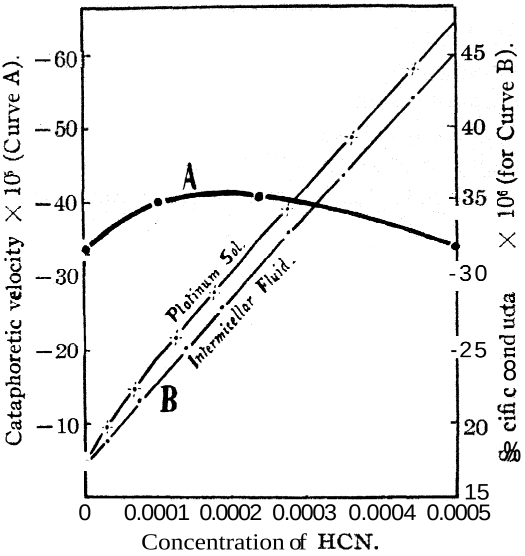

Fig. 3.—Curve A shows the change in cataphoretic velocity with concentration (6-potential = cataphoretic velocity × 187.1). Curve B shows the change in conductivity with concentration both for the platinum sol and for the intermicellar fluid.

TABLE II

CHANGE IN THE SPECIFIC CONDUCTIVITY ON THE ADDITION OR HYDROCYANIC ACID. TEMPERATURE, 18°

Platinum sol		Intermicellar fluid	
Concn. of HCN	k	Concn. of HCN	k
....	17.36	....	17.18
0.000028	19.72	0.000028	18.92
.000069	22.42	.000073	21.52
.000125	25.83	,000137	25.13
.000177	28.98	,000188	27.94
.000277	34.62	,000278	32 93
.000366	39.49	,000353	36.88
.000448	43.89	.000449	42.01

lie below that of the intermicellar fluid. The opposite was found to be the case, for the platinum sol curve always lay above that of the comparable solution. Hence at all concentrations the decrease in conductivity due to the removal of hydrocyanic acid is completely overshadowed by some action which increases the conductivity. Two explanations of the latter action suggest themselves.

First, although hydrocyanic acid is a weak electrolyte, its combination at the surface may, and probably does, result in the formation of complex ionogens which are strong and highly ionized.[28] The increase in conductivity could then be attributed to the ionization of these fresh surface ionogens. Now it has been shown that pure platinum sols, with a cataphoretic velocity of **33.8** X 10^{-5} cm. sec. volt cm., do not contribute any measurable fraction of the conductivity; it may safely be concluded that when the velocity is increased to 41 X 10^{-5} units, the conductivity due to the particles (and their contra ions) would still be of a negligible order of magnitude.

The second explanation, which is probably correct, is that when the hydrocyanic acid combines with the surface, some (or even the whole) of the surface hexahydroxyplatinic acid is displaced. Such replacement is not unusual[29] and is due to a difference in affinity of the surface for the substances concerned. The removal of the weakly ionized hydrocyanic acid from solution, and its replacement by the strong acid $H_2Pt(OH)_6$, serves to explain the increase in conductivity found. If we assume that the whole of the increase, namely, 2 gemmhos[30] at high concentration, is due solely to this effect, then calculation shows that for one liter of sol, 0.000007 equivalent of $H_2Pt(OH)_6$ is replaced. This approaches the total amount of the hexahydroxy acid held at the surface as given by the barium chloride figures, namely, 0.000011 equivalent. Making allowance for hydrolytic cleavage in the latter case, it would appear that at higher concentrations the hydrocyanic acid replaces the greater part (and maybe all) of the bound platinic acid. Such effects in the presence of other surface active substances, particularly sodium hydroxide, must not be overlooked.

Until further experimental evidence is at hand, it is not considered advisable to present any conclusions which may be drawn connecting these surface actions with the catalytic phenomena.

The author is indebted to the Trustees of the Endowment Fund of the Council for Scientific and Industrial Research of the Commonwealth of Australia for grants toward the purchase of platinum used in these investigations.

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[28] Compare the results obtained with hydrogen sulfide by Rabinowitsch and Kargin, *Z. physik. Chem.,* **143,** 21 *(1929).*

[29] See, for example, Warburg, *Z. Physiol.,* **76, 331** (1911).

[30] **A** gemmho is a reciprocal megohm.

summary

The general behavior of colloidal platinum as a typical acidoid sol is discussed from the point of view of more recent work.

Experiments are quoted which show that the whole of the colloid surface appears to be coated with a layer of oxidized platinum. On passing hydrogen the oxide layer is reduced **and** the acidoid properties disappear. On repassing oxygen or air the acidoid properties are recovered.

The $H_2Pt(OH)_6$ combines with part of the surface oxide to form Werner compounds, which act as the stabilizing surface ionogens.

The rest of the oxidized surface remains uncombined, but exhibits the properties of an acid oxide.

All the reactions of colloidal platinum are intimately connected with the acidic nature of the surface. They may be divided into three classes: ionic replacement, complex or salt formation and hydrolytic cleavage.

The general action of acids, bases and salts is interpreted in terms of these three reactions.

It is shown that hydrocyanic acid increases the charge carried by the colloid particle, and at the same time appears to displace the surface hexahydroxyplatinic acid.

THE UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MICHIGAN STATE COLLEGE]

THE DENSITY OF WATER ADSORBED ON SILICA GEL[1]

BY DWIGHT T. EWING AND CHARLES H. SPURWAY

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It is well known that water adsorbed on a surface of a solid has undergone a thermodynamic change in state and that it is held to the surface by a force of great magnitude which may be expressed in terms of pressure, compressibility, etc. Among the early investigators to advance this idea were Rose,[2] Jungh[3] and Parks.[4] That silica gel holds adsorbed water as if under a high pressure is also more recently confirmed by data on the heat of adsorption of water by Lamb and Coolidge,[5] and Patrick and Grimm.[6] The object of this investigation was to measure by a direct method the volume of water adsorbed on silica gel and to determine its density when present in small amounts.

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[1] This paper represents the thesis submitted by Charles H. Spurway to the Graduate School of the Michigan State College, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[2] Rose. Ann. *Phys.*. 73, 1 (1849).

[3] Jungh. Ann. *Phys.* Chem.. 125,292 (1865).

[4] Parks, *Phil. Mag.*, 4,220 (1902); 5,517 (1903).

[5] Lamb and Coolidge. THIS JOURNAL, 42, 1146 (1920).

[6] Patrick and Grimm, *ibid.*, 43,2144 (1921).

Ikerman[7] and one of us have measured the adsorption of helium on an active silica gel and it was found that no appreciable quantity was adsorbed until the temperature was lowered to near that of liquid oxygen. It seemed advisable, therefore, to use this gas as a medium for determining the various volumes necessary in this investigation.

Experimental Procedure

Apparatus.—The design of the apparatus is similar to that heretofore used for adsorption experiments. All glass parts are of pyrex glass. The form of the gel bulb A (Fig. 1) permits heating the gel by means of a cylindrical, electrical heating unit placed on from the top, and which could be replaced bv a constant temperature bath as outlined in the illustration. B is a calibrated gas pipet used for measuring and admitting known volumes of helium to the gel bulb. Air pressure at G and suction at D permit rough adjustment of mercury levels in the apparatus for the several operations. Fine adjustments of mercury levels for the cathetometer readings were obtained by means of the short rubber tubing at J operated by means of a pinchcock. For more accurate readings, the calibration marks on the stem of the gas pipet and the gel bulb are vertical scratches, read from the lower points, instead of the ordinary cross-etchings. The water was admitted to the gel by means of the side tube E, which is shown as containing a glass capsule of water and a soft iron rod enclosed in glass.

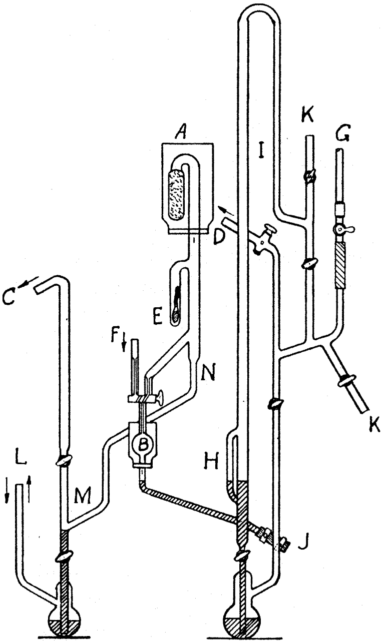

Fig. 1.—Adsorption apparatus.

Purification of the Helium.—The helium used in this work was furnished by the United States Bureau of Mines. As the experimental operations were conducted under conditions requiring adsorbable gases to be absent from the helium, it was necessary to purify the helium by removing these gases. The apparatus shown in Fig. 2 was designed for this purpose. A discussion of the operations performed in purifying the helium will also describe the uses of the different parts of the apparatus. After the apparatus was made ready for use, the "norite" charcoal bulbs O and P were heated to 500° by means of electrical heating units surrounding the bulbs, and the apparatus was evacuated through Q to activate the charcoal. The heating and evacuating occupied three periods of time of six hours each. After the minimum pressure was held for several hours, tube Q was sealed off, charcoal bulb O was surrounded with liquid air in a Dewar flask and when the temperature equilibrium was thought to have been attained, helium gas was allowed to flow slowly from the tank R through O to atmospheric pressure as was shown by the barometric gage S. Tube T was then sealed off, the liquid air was transferred to P and the helium was passed back and forth slowly through P seven times. The helium was finally stored in flask U and tube V sealed off. During all these operations mercury stood in tube F to the upper bend.

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[7] Ikerman, Master of Science Thesis, Michigan State College, 1927.

Preparation of the Gel.—A sample of commercial Patrick's gel was passed over a 2-mm. round-hole screen and the particles held on the screen were carefully sorted. saving only the clear, uncontaminated particles. The dark-colored, opalescent and chalky particles were discarded. After sorting the gel, it was carefully dusted by rolling it on a piece of black velvet cloth.

Filling the Wafer Capsule.—Especially purified water was used from which the air and other gases had been removed by heating and evacuating. A piece of glass tubing of suitable size was drawn to a capillary in the middle section and weighed. The capsule end was then filled nearly full with the water and evacuated for several minutes to the vapor pressure of water at the operating temperature. Maintaining the pressure, the top was sealed off at the capillary, the whole reweighed and the weight of the water determined.

Temperature Control of Constant Temperature Bath.—This temperature control was effected by means of a 25-watt electric light bulb, operating against a stream of cool air bubbled through the water of the bath to obtain circulation of the water, and connected through a relay to a thermo-regulator set to maintain a temperature of 25.020 ± 0.004° as measured by a Beckmann thermometer.

Barometer.—The atmospheric pressure readings were obtained from a barometer made from heat-treated evacuated pyrex tubing and filled with purified and evacuated mercury. Filling the tube with mercury was accomplished by breaking off the lower end of the evacuated tube under the mercury. After continuing the evacuation for some time to the lowest pressure obtainable and with further heat treatment of the upper end of the tube, the barometer was sealed off from the apparatus and attached to the apparatus rack near the manometer.

Pressure Readings.—All of the pressure readings were made with a cathetometer calibrated to read to 0.05 mm. The mercury column of the manometer was always forced upward to the mark, and the mercury columns of both the manometer and barometer were carefully equilibrated before reading them.

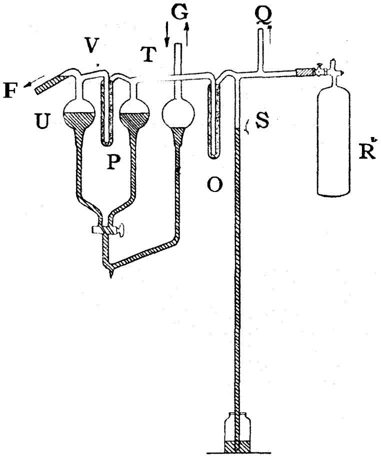

Fig. 2.—Apparatus for purification of helium.

Operation of Apparatus.—The minimum pressure obtained in the cool apparatus, and for all of the determinations requiring low pressure, was of the order 1 by 10^{-5} mm.

The silica gel, prepared as previously described, was admitted to the gel bulb through the bulb stem before sealing to the apparatus. After sealing the gel bulb containing the gel to the apparatus, the gel was heated to 250" and evacuated for several hours, the water tube E not being attached to the apparatus. When a satisfactory low pressure was obtained, the mercury trap M was closed and the mercury raised to N. Helium was then drawn from the storage flask into the gas pipet B and the volume measured in cc. at 25.02° and 760 mm. The helium was then admitted to the gel bulb, pressure readings were taken on it at certain intervals of time, and the volume not occupied by dry gel was determined under equilibrium conditions after several days. This volume subtracted from the volume of the gel bulb, determined by helium in the same manner, gives the volume of the dry gel. In the next step the mercury was drawn out of the manometer, and the water tube E, containing a known weight of water, was attached to the gel bulb stem below the calibration mark. Heat was again applied to the gel (250°), the gel evacuated to low pressure to remove the helium previously used, and the mercury elevated to fill the manometer up to the water tube inlet. The water capsule was then broken by raising the iron weight by means of an electromagnet and releasing it to fall on the capillary end of the water capsule. On breaking the water capsule, the water vapor was drawn rapidly into the gel, requiring about two hours for the largest quantity of water used (2.5667 g.) to disappear from the water tube, but the gel was allowed to stand for one day before further operations, in order to attain better equilibrium conditions. After sealing off the water tube close to the gel bulb stem, another volume of helium was then admitted to the gel bulb and the volume not occupied by gel and water was determined. From these results the volume and density of water adsorbed on the gel were calculated. The weight of the dry, evacuated gel was determined by sealing off the gel bulb under low pressure and making the requisite weighings.

TABLE I

PRESSURE READINGS OF HELIUM IN THE GEL BULB

Time, days	Press. on helium in gel bulb alone, mm.	Press. on helium in gel bulb with dry gel, mm. 1	2	3
1		501.35		511.55
2	750.15		502.95	511.10
3	749.70		502.85	510.70
4			502.75	510.80
5	749.40			
6		500.25	502.70	510.70
7	749.40	500.30		
8	749.35			

Time, days	Press. on helium in gel bulb with gel and different amounts of adsorbed water, mm. 2.5667 g.	2.1095 g.	1.6867 g.	0 6357 g.	0.4017 g.
1		524.70	532.60	513.10	
2	543.90		532.55		516.55
3	544.00	524.10	532.70	512.55	516.35
4	543.90	524.00	532.65	512.30	
5	543.85			512.15	
6	543.55			512.05	
7				512.10	
8					
9	543.00				
10	543.05				
11	543.00				516.30
13					516.25

TABLE II

VOLUME OF GEL BULB AND VOLUME OF DRY GEL

All volumes calculated in cc. at 25.02° and 760 mm.

	Vol of He taken, *cc.*	Equil. press., mm.	Vol of gel bulb, *cc.*	Vol. of He in gel bulb, *cc.*	Vol of dry gel, cc.
	68.850	749.35	69.826		
a	34.325	500.25		52.147	17.679
b	34.498	502.70		52.154	17.672
c	35.044	510.70		52.150	17.676

Average vol. of dry gel	17.676 cc.
Wt. of dry gel *in vacuo*	38 6495 g.
Density of dry gel	2.1866 ± 0.0006

TABLE III

MEAN DENSITIES OF ADSORBED WATER

Wt of ads. water, g.	Vol of He taken, cc.	Equil. press, mm.	Vol. of He in gel bulb, cc.	Vol. of gel and water, cc.	Vol. of ads. water, cc	Density of ads. water
2.5667	33.869	543.00	47.404	22.422	4.746	0.5408
2.1095	34.205	524.00	49.610	20.216	2.540	.8305
1.6867	35.401	532.55	50.510	19.316	1.640	1.0285
0.6357	34.719	512.05	51.531	18.295	0.619	1.0270
.4017	35.157	516.25	51.756	18.070	.394	1.0195

Discussion

The accuracy of the results depends on the correlation of equilibrium conditions of the several pressure determinations. In order to meet these conditions as nearly as possible, the pressure readings were taken until the daily change in pressure was small, in most cases 0.05 mm.

An interesting phenomenon was observed when the largest quantity of water was admitted to the gel. Immediately on breaking the water capsule, the water vapor was drawn into the gel with sufficient force to raise the iron weight (9.245 g.) and hold it against the top of the water tube until the water was nearly all in the gel. In some cases the water froze in the water tube. On adsorbing the first quantity of water vapor, the gel became warm at the top and the heat, passing downward through the gel, could be traced with the hand. Only a few minutes were required for the heat to become distributed throughout the gel. From this heat effect it is concluded that the water vapor was evenly distributed over the gel surface.

There is a close correlation between the density values for the 1.6867 g. and 0.6357 g. of adsorbed water, indicating one phase of water on the gel. The density value for the smallest quantity of water used is somewhat lower, probably because of the greater experimental error due to the small volume. The mean density values for the two larger quantities of adsorbed water are less than the density of liquid water at the operating temperature, indicating the presence of three water phases: compressed water, liquid water and water vapor. This water vapor, however, exerts only a low vapor pressure; hence, all three forms of water are held on the gel under pressure. A sudden break occurs in the mean density curve (Fig. 3) at a point near the value for 1.6867 g. of adsorbed water.

No measurable vapor pressure was shown on the manometer by the three smallest quantities of adsorbed water, but the two larger quantities gave a vapor pressure of 4 mm. each. The calculated volume of water vapor in the gel bulb corresponding to this pressure, however, was not significant in these determinations. These vapor pressure measurements show that the vapor pressure of the adsorbed water is very low.

By a calculation based upon the volume of the adsorbed water in the runs where the silica gel contained 1.6867 g. or 0.6357 g. of water, and a correlation of Bridgman's compressibility data ("International Critical Tables," Vol. III, p. 40), it is shown that in these cases the pressure on the adsorbed water is of the magnitude of 750 atmospheres.

TABLE IV

ERRORS

Mean density	0.5408	0.8305	1.0285	1.0270	(1.0195)
Exptl. errors	* .0005	± .0017	±0.0031	±0.0083	±0.0129
He ads. errors	− .0027	− .0065	− .0099	− .0099	− .0102

The greatest probable error in these determinations was in reading the barometer and manometer and was calculated to be ±0.025 mm. on each reading or ±0.05 mm. on both in case the error was positive on one reading and negative on the other. Applying this error to the data, the values given as experimental errors in Table IV were obtained. The possible error due to the absorption of helium in the water was calculated from the data of Lannung[8] assuming that the water adsorbed on the silica gel absorbed helium to the same extent as does liquid water. This assumption is improbable, however, especially where the water is held under great pressure.

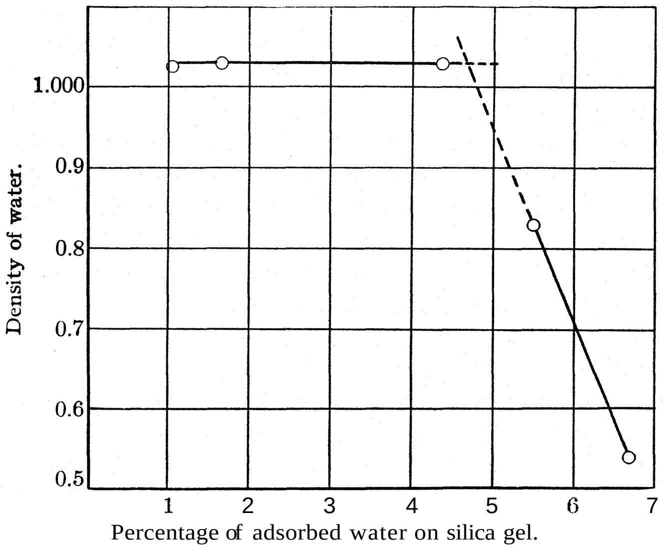

Fig. 3.—Mean density curve.

A noticeable drift occurs in the pressure readings with time (Table I), varying from 0.05 mm. with 1.6867 g. of water on the gel to 1.05 mm. both with dry gel and 0.6357 g. of adsorbed water. As this drift also occurs with helium only in the gel bulb, it must be due chiefly to adsorption of helium on the inner walls of the gel bulb or absorption of helium in the

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[8] Lannung. THIS JOURNAL, 52, 68–80 (1930).

mercury exposed to the helium. Provided this drift was caused by adsorption of helium on the gel bulb only, it should be nearly the same in all cases as the gel bulb was heated and evacuated each time before admitting the helium. The differences in this drift may be caused partly by mercury surfaces in the manometer containing more or less absorbed helium when exposed to the helium in the gel bulb. In the three determinations of volume of dry gel made before the admissions of 1.6867 g., 0.6357 g. and 0.4017 g. of water, the variations from the mean were only +3 and —4 parts in 17,676, although the drifts in the pressure readings were 1.05 mm., 0.25 mm. and 0.85 mm., respectively. The computations were made, therefore, on the basis of the volumes determined directly with helium, using the lowest pressure readings, and considering that a stable pressure equilibrium was reached in each case.

Summary

Values were obtained for the density of water adsorbed on silica gel by volume measurements using a gas dilatometer with helium as the inactive gas. For small quantities of water up to 4.36% these measurements showed that the density of water adsorbed on silica gel at 25.02° is greater than the density of liquid water at the same temperature.

EAST LANSING, MICHIGAN

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

THE THERMODYNAMIC PROPERTIES OF MOLTEN SOLUTIONS OF LEAD CHLORIDE IN LEAD BROMIDE

BY E. J. SALSTROM AND J. H. HILDEBRAND

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The investigation described in this paper represents a continuation of the plan begun several years ago in this Laboratory by Hildebrand and Ruhle[1] of studying the thermodynamic properties of fused salt solutions. There were two disturbing factors involved in that investigation, first, the system studied, solutions of lead chloride with potassium chloride, was somewhat complex, as indicated by the existence of several solid compounds; second, the chlorine electrode was produced by polarization, a procedure that did not guarantee its reversibility. In the present investigation a system has been selected, lead bromide with lead chloride, which, according to Monkmeyer,[2] shows no evidence of compound formation in the solid state. The freezing point varies linearly with the composition, indicating a continuous series of solid solutions. The second complication mentioned above has been avoided by our success in constructing a reversible bromine electrode suitable for use under these conditions.

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[1] Hildebrand and Ruhle, THIS JOURNAL, 49, 722 (1927).

[2] K. Monkmeyer, *Neues Jahrbuch.* 22, 1 (1906).

Further interest attaches to this system because Professor W. C. Bray[3] made a suggestion in 1908 that the freezing points of this system should offer an opportunity to determine the extent of ionization. Unfortunately the existence of solid solutions invalidates any simple conclusion from the freezing points and makes desirable the use of some other measure of partial molal free energy. Since the completion of our investigation there have appeared measurements of the partial vapor pressures of this system carried out by Jellinek and Bolubowski.[4] These will be referred to later.

Experimental Part

A. Materials and Apparatus.—The lead chloride was from commercial sources of high purity. The lead bromide was prepared by precipitation from ammonium bromide and lead acetate solutions in **0.001** N hydrobromic acid. The precipitate was washed repeatedly by decantation with a dilute solution of the acid, and dried by suction on a filter. It was then boiled in the acid solution, cooled, washed again by decantation, dried by suction and twice again subjected to this procedure. Tests then showed it to be free from ammonium salts. It was finally dried in a furnace at 130° for over twelve hours. Hydrogen bromide gas was prepared directly from its elements by passing hydrogen and bromine over a heated catalyst of platinized asbestos. The hydrogen used was especially prepared in this Laboratory by the electrolysis of water. It was freed from oxygen by passing it over a hot nickel catalyst, and from water by passing, first, through a sulfuric acid drying tower, and finally over phosphorus pentoxide. The bromine used in the preparation of hydrogen bromide was freed from chlorine and water by standing over powdered anhydrous calcium bromide and then twice distilled from calcium bromide. The bromine used for the electrode in the cell was generated by electrolysis of molten lead bromide. The hydrogen chloride gas was produced by dropping concentrated sulfuric acid on pure concentrated hydrochloric acid, and was dried by bubbling through a tower containing concentrated sulfuric acid. The molten lead used as an electrode was prepared by electrolysis of pure molten lead bromide.

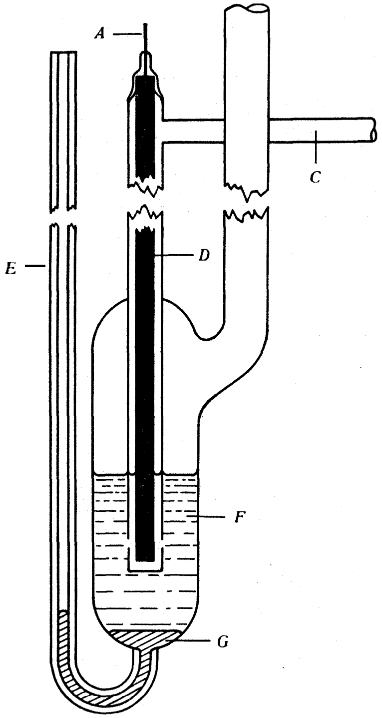

Fig. 1.—Cell container.

The cell containers were made of pyrex glass of cylindrical form, **2–3** cm. in diameter and about **30** cm. long, as shown in Fig. **1**. Tungsten wires with copper leads were

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[3] *Cf.* Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923,** p. **219;** see also Goodwin and Kalmus, *Phys. Rev.,* **28,** 1 **(1909);** *W.* C. Bray, Z. *physik. Chem., 80,251* (1919).

Jellinek and Bolubowski, *Z. physik. Chem.,* Abt. A, **147,461 (1930).**

sealed into the tube, E, so as to make contact with the molten lead, G. The positive electrode, D, was a graphite rod 6–10 mm. in diameter, its size depending on the number of heat treatments it had undergone. These rods were sealed into the cells by means of platinum wire leads, A. Tube C served as an inlet for bromine vapor. The large open tube was first used as an opening for charging the cell with salt and metal, after which it was sealed onto a bromine trap, to serve as an exit for bromine. The bromine generator, made of pyrex glass and having positive and negative poles, respectively, of graphite and tungsten wire, was larger than this cell, but similar in construction.

The thermostat consisted of a large electrical resistance pot furnace of high heat capacity and well insulated. The thermostat bath was a mixture of molten lead and tin. An efficient mechanical stirrer kept the bath at a uniform temperature. The pot and stirring fan were of cast iron, and were protected from the solvent action of the bath by several coats of "Insa-lute" cement.

The temperature was measured by two platinum–platinum-rhodium thermocouples, standardized by the U. S. Bureau of Standards. During the course of the investigation the thermocouples were repeatedly checked against each other and were found accurate to within 0.5°. All electromotive force measurements were made on a Leeds–Northrup type K potentiometer.

B. Method of Procedure.—The graphite rods used as electrodes in the cell and generator were first treated for about twenty-four hours with bromine gas under several atmospheres' pressure at 600°. They were then heated in the oxygen flame to a bright yellow heat until no more fumes were evolved, and allowed to cool in an atmosphere of bromine. These rods were used over and over again, but with each new cell or generator the glowing and cooling process was repeated. The only observed difference between graphite rods thus treated and those untreated was that in the former case equilibrium was reached in from one to two hours, while otherwise eighteen to twenty hours were required.

The generator was charged with pure lead bromide and placed in a small cylindrical electrical resistance furnace kept at about 450°. The cells were first charged with pure lead in sufficient amounts to cover completely the sealed-in tungsten wires. Weighed amounts of lead chloride and lead bromide were then added, and the cell was lowered into the thermostat bath and sealed in series with the bromine generator. All connections were of glass only. Stopcocks, where they could not be dispensed with, were lubricated with concentrated sulfuric acid, since bromine attacked the various greases tried, causing them to harden. No openings to the air were permitted except in the bromine exit tube, where a trap of liquid bromine was inserted.

The lead bromide in the generator, and also in the cell, when it contained lead bromide only, was freed from moisture, oxides and hydrolysis products occasioned by the filling and sealing up process by bubbling dry hydrogen bromide gas through the melt for an hour and forty minutes. Without such treatment, the fluctuations in e. m. f. were quite marked. Equilibrium was reached in from one to two hours. Prior to taking each reading, the thermostat was kept constant within one or two degrees for sufficient time to insure constant e. m. f. Each cell was in this way measured at twenty- or thirty-degree intervals over the whole temperature range several times. Ascending and descending series were in complete agreement.

The cells containing solutions of lead bromide and lead chloride were cleaned out with hydrogen chloride gas instead of with hydrogen bromide, since the reaction

$$PbCl_2 + 2HBr = PbBr_2 + 2HCl$$

was found experimentally to proceed almost quantitatively as written.

Using the free energy of formation of lead bromide given in this paper, the free energy value of lead chloride, given by Wachter and Hildebrand in a paper shortly to appear as −**58,720** cal., and the free energy equations for the formation of hydrogen chloride and hydrogen bromide gas

$$\text{for HCl, } \Delta F = -21{,}870 + 0.45\,T\ln T - 0.000025\,T^2 - 5.31\,T$$
$$\text{for HBr, } \Delta F = -11{,}970 + 0.45\,T\ln T - 0.000025\,T^2 - 5.74\,T$$

as given by Lewis and Randall,[5] we have calculated the free energy change of this reaction to be −**8050** cal. at 500°. That the reverse reaction is negligible in effect was proved by passing hydrogen chloride gas through the cell for thirty minutes, then measuring the e. m. f. over a range of temperatures, again passing in hydrogen chloride for thirty minutes and again determining the e. m. f.–temperature curve. No difference was observed in the two sets of readings.

To test the effect of polarization on the e. m. f. of the pure lead bromide, the cell was electrolyzed by a current of **0.1** to **0.15** ampere for one hour without shutting off the bromine stream from the generator. After such polarization, no change in the readings of the cell was observed. However, when an electrolyzing current of *2* to **3** amperes was used, the e. m. f. immediately after electrolysis was from two to three centivolts higher, thus being more in accord with the results of Lorenz and Czepinski,[6] obtained by a polarization method.

The cells used involved a thermoelectric effect. To correct for this, cells were made up, identical with those used with molten salts with the exception that the contact between tungsten and graphite was in this case made by a platinum wire instead of molten salts. The e. m. f. of these cells, placed in the thermostat in the same position as the other cells, was measured over a temperature range, using two types of graphite rods, some treated as previously described, and others untreated. These gave identical and very reproducible e. m. f.'s.

Since it was hoped that lattice energy considerations would prove useful in interpreting the experimental results, density determinations were made by a pycnometer method, using pyrex bulbs of about 15-cc. capacity and having a capillary stem of **3** mm. The problem of filling these bulbs with the molten salts made a smaller capillary impracticable. The data of Peters and Cragoe[7] indicate that the coefficient of expansion for pyrex glass can be satisfactorily applied up to a temperature of 500°.

Experimental Results

Measurements for this system are given in Table I and plotted in Fig. **2.**

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[5] Lewis and Randall, Ref. 3.

[6] Lorenz, "Die Elektrolyse geschmolzener Salze," Dritte Teil, p. 207, "Elektromotorische Krafte," Knappe, Halle a.S., 1906.

[7] Peters and Cragoe, Bur. of Stand. *Sci. Papers,* 16,449–487 (1920).

TABLE I

$Pb/PbBr_2,\ PbCl_2/Br_2$

Mole fraction of $PbBr_2$	Temp., °C.	E. m. f. observed, volts	Mole fraction of $PbBr_2$	Temp., °C.	E. m. f. observed, volts
1.000 C	438.3	1.0692	0.600 E	445.3	1.0888
1.000 B	443.5	1.0665	.600 E	468.5	1.0765
1.000 A	451.0	1.0615	.600 E	493.9	1.0626
1.000 A	453.0	1.0601	.600 E	514.2	1.0514
1.000 C	465.6	1.0525	.600 E	531.4	1.0422
1.000 B	468.0	1.0516	.600 E	535.5	1.0400
1.000 A	484.3	1.0416	.600 E	552.6	1.0304
1.000 A	496.2	1.0330	.600 E	578.9	1.0160
1.000 C	501.1	1.0306	.600 E	583.6	1.0136
1.000 C	517.1	1.0215	.500 F	450.1	1.0957
1.000 A	520.0	1.0200	.500 F	464.3	1.0879
1.000 B	527.6	1.0156	.500 F	488.2	1.0750
1.000 A	536.0	1.0100	.500 F	516.2	1.0599
1.000 A	556.0	0.9979	.500 F	536.3	1.0490
1.000 B	561.2	1.9945	.500 F	580.2	1.0249
1.000 A	576.0	1.9856	.450 G	448.0	1.1053
0.800 D	450.7	1.0731	.450 G	475.7	1.0897
.800 D	486.3	1.0523	.450 G	501.3	1.0756
.800 D	515.6	1.0350	.450 G	507.5	1.0730
.800 D	551.6	1.0148	.450 G	528.4	1.0616
.800 D	576.5	1.0002	.450 G	553.9	1.0468
			.450 G	584.0	1.0308

Three cells were run for pure lead bromide, cell **A** containing a graphite electrode treated as above described and cells B and C with untreated graphite rods. Each was run over the whole temperature range of 450 to 580°. In no case was a deviation from a straight line observed in excess of 0.5 millivolt, and the average deviation was less than 0.2 millivolt. The cells containing solutions of lead bromide with lead chloride were found to give equally accurate and reproducible results. The cells containing pure lead bromide yield the relation that $\Delta F = -69270 + 28t$ over the range studied.

The values of Lorenz and Czepinski for the e. m. f. of pure lead bromide obtained by polarization deviate from their smoothed out curve by as much as 5 to 6 millivolts. The curve chosen by them to smooth out their results is about 0.024 volt higher than ours at 450° and 0.030 volt higher at 550°. However, since they carried out their experiments in open vessels and, as far as we can determine, made no effort to eliminate impurities due to oxidation and hydrolysis, we can readily understand why their figures should differ considerably from those herein given.

To determine whether we were actually dealing with a reversible electromotive force, and one which is in accord with the assumed cell reaction, we studied the effect of pressure changes on the e. m. f. of the cell. The bromine passing through the cell was allowed to escape against a reduced external pressure. Table II gives the results. It will be seen that the observed e. m. f.s agree to 0.2 millivolt or better with those calculated by the aid of the usual formula. We may therefore claim a high degree of accuracy for this electrode.

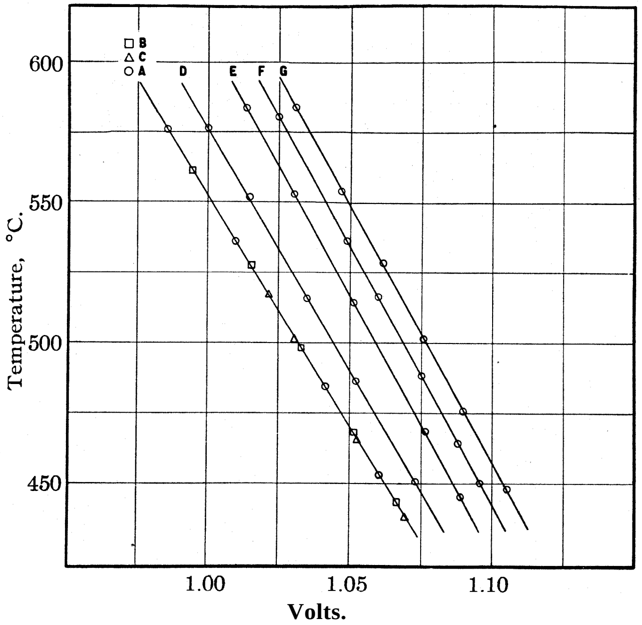

Fig. 2.—Temperature, e. m. f. and composition relations of the cells Pb/$PbBr_2$, $PbCl_2$/Br_2. Mole fraction of lead bromide in A, B and C is 1.000, D is 0.800, E is 0.600, F is 0.500 and *G* is 0.450.

TABLE II

THE EFFECT OF PRESSURE UPON THE BROMINE ELECTRODE IN THE LEAD BROMIDE CELL

Pressure, cm. of mercury	74.96	60.04	43.80	55.21	60.8
Temperature, °C.	443.3	438.6	442.3	443.3	441.7
E **(obs.)**	1.0671	1.0634	1.0511	1.0576	1.0609
E **(calcd.)**	1.0671	1.0632	1.0510	1.0576	1.0611

It was found that when the concentration of lead chloride in the molten solution reached a mole fraction of 0.6, the reaction

$$PbCl_2 + Br_2 = PbBr_2 + Cl_2$$

first became noticeable by a gradual falling off in the e. m. f. of the cell if observed over a period of twenty-four hours. Subtracting the free energy of formation of lead chloride from its elements, —58,720 cal. at 500°, from that for the formation of lead bromide from its elements herein given, we arrive at +11,090 cal. as the free energy change of this reaction when each substance is at unit activity. Using this value and assuming that the activities of the salts are proportional to their mole fractions, we have calculated the partial pressure of chlorine at 0.6 mole fraction lead chloride to be less than 0.002 atmosphere at equilibrium. This small pressure might be considered negligible were it not for the fact that chlorine is constantly being swept out as fast as formed by the bromine stream passing through the cell. That the above reaction does not occur appreciably at lower concentrations of lead chloride is shown by the fact that no falling off in the e. m. f. with time is discernible, even though allowed to run for several days. In view of the above considerations, we do not give any measurements upon cells containing lead chloride above 0.55 mole fraction.

In order to determine how the molal volumes of the solutions vary in going from pure lead bromide to pure lead chloride, density determinations were made of the pure salts and solutions of them. The results are given in Table III. The density value given for lead chloride in Table III at 500' was obtained by extrapolation of the molal volumes–composition curve, since the salt freezes at 501°. Extrapolating the density values obtained by Lorenz, Frei and Jabs,[8] we obtain 4.897 for lead chloride at 507° and 5.45 for lead bromide at 500° compared to our measured values of 4.879 and 5.4735, respectively. Since we have extrapolated the values of these investigators below the region for which they were given as valid, the agreement is quite satisfactory.

TABLE III

RELATIONS BETWEEN COMPOSITION, DENSITY AND MOLAL VOLUMES OF LEAD BROMIDE–LEAD CHLORIDE SOLUTIONS AT 500°

Mole fraction lead bromide	1.000	0.800	0.600	0.500	0.450	0.200	0.000
Density of soln.	5.4735	5.381	5.2537	5.2013	5.1219	5.027	4.887 (extrapolated)
Obs. volume of 1 mole of soln. in *cc.*	67.05	64.86	63.01	61.92	61.335	58.70	56.75 (extrapolated)
Calcd. on basis of additivity	67.05	64.97	62.91	61.88	61.34	58.79	56.75

Discussion of Results

To show the effects of both temperature and composition upon the thermodynamic properties of the salt solution we have proceeded as follows. The plot shown in Fig. 2 was made upon a large scale and the values of the e. m. f., E, determined for each solution at the temperatures 450, 500 and 550'. Using then the relation $\Delta F_1 = -23{,}070\ NE$, where N is the number of equivalents per mole, here 2, we calculate ΔF_1, the free energy of formation of lead bromide in calories, from molten lead and bromine vapor at 1 atmosphere. This varies with the mole fraction of $PbBr_2$, N_1, and we will write ΔF_1° to denote pure lead bromide. The partial

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[8] Lorenz, Frei and Jabs, *Phil. Trans. Royal Society,* 7,468 (1908).

molal free energy of lead bromide in a solution, $\bar{F}_1$, is then $\bar{F}_1 = \Delta F_1 - \Delta F_1^\circ$. The entropy of formation, ΔS_1, is given in calories per degree by $\Delta S_1 = 23{,}070\ N\ dE/dT$, and the partial molal entropy $\bar{S}_1 = \Delta S_1 - \Delta S_1^\circ$. The heat of formation is $\Delta H_1 = \Delta F_1 + T\Delta S_1$ and the partial molal heat $\bar{H}_1 = \Delta H_1 - \Delta H_1^\circ$. The activity of lead bromide in its solutions, a_1, taking pure lead bromide as the standard state, is calculated by the relation $\bar{F}_1 = RT \ln a_1$. By dividing the activity by the mole fraction of lead bromide, the activity coefficient, γ, is obtained.

The values so calculated are given in Table IV, and in Fig. 3 are shown, in Curve A, the values of $-\bar{F}_1$ at 500° plotted against log $(1/N_1)$, where N_1 is the mole fraction of lead bromide. In order to see how these values agree with simple assumptions regarding ionization, we will assume, first, that both salts are un-ionized, and that the activity of lead bromide is proportional to its mole fraction. This gives curve B, Fig. 3, much lower than the observed. This corresponds to a negative deviation from Raoult's law, *i. e.*, the activity is less than the simple mole fraction. This can be seen quite clearly by comparing the values of a_1 in the table with the corresponding values of N_1. This result does not accord with the measurements of Jellinek and Bolubowski,[4] who found Raoult's law obeyed by the vapor pressures at temperatures from 660 to 780°. We are at a loss to explain the discrepancy, as neither the difference in the temperature range nor departure of the vapors from the gas laws would seem to be sufficient to account for it.

TABLE IV

ENERGY RELATIONS OF LEAD BROMIDE, WHEN DILUTED WITH LEAD CHLORIDE

N_1	1.000	0.800	0.600	0.500	0.450
$dE/dT \times 10^6$ (volts/deg.)	−607	−580	−548	−544	−542
ΔS_1 (cal./deg.)	−28.01	−26.77	−25.29	−25.10	−25.01
$\bar{S}_1$ (cal./deg.)	0	1.24	2.72	2.91	3.00
450°, E (volts)	1.0624	1.0736	1.0866	1.0959	1.1038
450°, ΔF_1 (cal.)	−49030	−49540	−50140	−50570	−50940
450°, $\bar{F}_1$ (cal.)	0	−510	−1110	−1540	−1910
450°, ΔH_1 (cal.)	−69280	−68890	−68420	−68720	−69020
450°, $\bar{H}_1$ (cal.)	0	+390	+860	+560	+260
450°, a_1	1.000	0.698	0.460	0.341	0.265
450°, γ	1.000	.873	.766	.682	.588
500°, E (volts)	1.0321	1.0447	1.0593	1.0687	1.0768
500°, ΔF_1 (cal.)	−47630	−48210	−48880	−49320	−49690
500°, $\bar{F}_1$ (cal.)	0	−580	−1250	−1690	−2060
500°, a_1	1.000	0.685	0.442	0.333	0.261
500°, γ	1.000	.856	.737	.667	.581
550°, E (volts)	1.0017	1.0156	1.0318	1.0415	1.0496
550°, ΔF_1 (cal.)	−46230	−46870	−47620	−48060	−48440
550°, $\bar{F}_1$ (cal.)	0	−640	−1390	−1830	−2210
550°, a_1	1.000	0.676	0.428	0.326	0.259
550°, γ	1.000	.845	.713	.652	.576

If we assume, second, that both salts are completely ionized, but that the partial substitution of bromide by chloride ion can be made without changing any of the interionic forces (an assumption which is obviously incorrect) then, if we take n_1 moles of $PbBr_2$ to n_2 moles of $PbCl_2$, we get $n_1 + n_2$ moles of Pb^{++}, 2 n_1 moles of Br^- and 2 n_2 moles of Cl^-. The activity of Pb^{++} would then be constant, unity; the activity of Br^- would be $n_1/(n_1 + n_2)$, the activity of $PbBr_2$ the former times the square of the latter, or N_1^2. This makes $-\bar{F}_1$ calculated upon this assumption, curve C in Fig. 3, just twice what it is on the former assumption. This agrees better with the observed values but is too high. We have, therefore, two alternatives, either to assume partial ionization, or, what is obviously preferable, to attempt to take into account the change in the interionic forces due to the substitution of the smaller chloride ion for the larger bromide ion. This we will postpone to a later communication where we will treat at the same time data obtained for other systems.

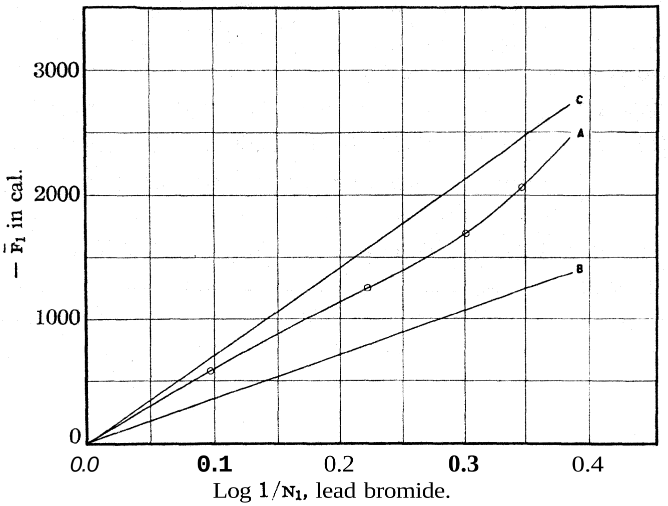

Fig. 3.—Change in free energy of lead bromide at 500° upon dilution with lead chloride: A, observed; B, calculated, no ionization; C, calculated, complete ionization.

Summary

1. A reversible and reproducible bromine electrode has been applied to the study of molten salts and their solutions.

2. Density determinations have been made on lead bromide and lead chloride and solutions of these at 500°. The molal volumes of these solutions have been found to be additive within the limits of experimental error.

3. The energy changes of molten lead bromide upon dilution with lead

chloride have been determined at mole fractions of lead chloride varying from 0 to 0.55, between the temperatures of 440 and 585'.

4. The free energy of formation of pure molten lead bromide was found to be $-69270 + 28t$ between $t = 450°$ and $t = 580'$.

5. The results have been discussed on the basis of simple assumptions regarding ionization, without taking into account the changes in interionic forces.

BERKELEY, CALIFORNIA

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

THE THERMODYNAMIC PROPERTIES OF MOLTEN SOLUTIONS OF LITHIUM BROMIDE IN SILVER BROMIDE

BY **E. J. SALSTROM** AND J. H. HILDEBRAND

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The work described in this paper is a continuation of the general program mentioned in the preceding article of collecting data necessary for a general study of molten salt solutions. Solutions of lithium bromide in silver bromide seem well suited to this investigation because their freezing point curves, investigated by Sandoninni and Scarpa,[1] show no evidence of complex salt formation which might add difficulty to any interpretation of the results. This is likewise true of silver bromide diluted with sodium bromide and with potassium bromide. A study of these latter two systems is now in progress in this Laboratory and when completed will furnish information on the influence of the size of the cation of the diluting salt upon the activity of the solvent.

Experimental Part

The silver bromide was prepared by precipitation from a solution of silver nitrate by ammonium bromide. It was washed repeatedly by decantation with a hot 0.001 N hydrobromic acid solution until freed from ammonium salts, then dried by suction on a filter, and finally in an oven at 130" for at least twelve hours. The lithium bromide was of high purity from commercial sources. It was freed from moisture by fusing the salt and bubbling dry hydrogen bromide gas through the melt for two hours. It was subsequently kept in a glass-stoppered bottle in a desiccator over anhydrous calcium chloride. The hydrogen bromide gas and the bromine used for the electrode in the cell were prepared as described in the preceding paper.

With the following exceptions, the apparatus and experimental procedure involved in the study of this system were essentially the same as those described for the lead bromide–lead chloride system. A pure silver

[1] **Sandoninni and Scarpa, *Atti.* accad. *Lincei,* 22, II, 517 (1913).**

wire inserted through the glass tube E, shown in Fig. 1 in the preceding article, served as the negative electrode. The amounts of lithium bromide added to the cells were but roughly weighed. Air and hydrolysis products were removed as before with a stream of dry hydrogen bromide gas continued in this case for at least two hours. After the run, the entire content of each cell was accurately weighed and dissolved in potassium cyanide solution. Measured portions were analyzed electrolytically.

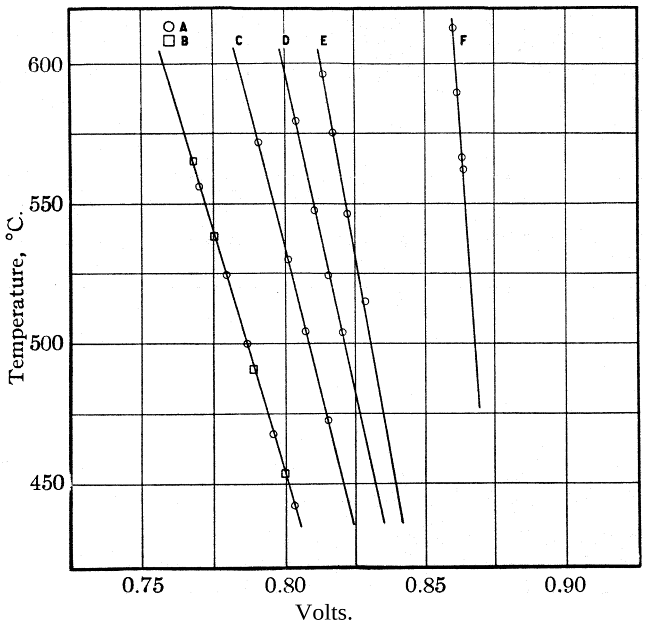

Fig. 1.—Temperature, e. m. f. and composition relations of the cells Ag/AgBr, LiBr/Br_2. Mole fraction of silver bromide in A and B is 1.0000, C is 0.5937, D is 0.4086, E is 0.2548 and F is 0.1100.

Since the cathode in these cells consisted of solid silver, the effect of any possible strains affecting its activity was investigated by polarizing the cell with 0.1 ampere for half an hour. The subsequent e. m. f. was identical with the previous one, hence at these high temperatures any strains such as are often found at room temperatures are negligible. The thermo-electric effect was measured as before, using in this case silver wire and graphite joined by a short platinum wire.

Measurements for this system are given in Table I and plotted in Fig. 1. The extreme deviation of the observed values from the straight lines drawn through them in Fig. 1 is 0.4 millivolt, and the average deviation is less than 0.15 millivolt.

Values for the e. m. f. of pure silver bromide have been obtained by

TABLE I

$Ag/AgBr, LiBr/Br_2$

Mole fraction of AgBr	Temp., °C.	E. m. f. observed, volt	Mole fraction of AgBr	Temp., °C.	E. m. f. observed, volt
1.000 A	442.3	0.8031	0.5937 C	567.7	0.7918
1.000 B	453.6	.8000	.5937 C	571.9	.7907
1.000 A	456.0	.7989	.4086 D	503.8	.8205
1.000 A	467.0	.7956	.4086 D	524.2	.8154
1.000 B	490.9	.7887	.4086 D	547.5	.8105
1.000 A	499.9	.7866	.4086 D	577.2	.8045
1.000 A	521.4	.7803	.4086 D	579.4	.8040
1.000 A	524.4	.7795	.2548 E	514.9	.8286
1.000 A	531.7	.7769	.2548 E	546.3	.8220
1.000 B	538.3	.7751	.2548 E	549.7	.8213
1.000 A	556.2	.7702	.2548 E	575.3	.8171
1.000 B	565.0	.7680	.2548 E	596.0	.8137
0.5937 C	472.5	.8153	.1100 F	562.0	.8639
.5937 C	501.8	.8081	.1100 F	566.3	.8635
.5937 C	504.2	.8072	.1100 F	589.5	.8616
.5937 C	529.8	.8011	.1100 F	612.8	.8603

Lorenz[2] by a polarization method where the molten salts were not protected from the air, nor, as far as we can determine, were any efforts made to remove oxidation and hydrolysis products. Their results deviate from a straight line by as much as 4 and 5 millivolts. The results chosen by this investigator to smooth out his results are at 450° about 8 millivolts higher than those observed by us, while at 550° they are 6 millivolts lower. Hence, while Lorenz's values are in fair agreement with those herein given, the slope of his curve is very different. Due to the higher melting point of lithium bromide, namely 556°, cells containing high mole fractions of this salt could be run only over a more limited range of temperatures. The experimental results were found to be reproducible within 0.5 millivolt.

The effect of a variable bromine pressure on the e. m. f. of the pure silver bromide cell was again studied. The excellent agreement between the observed and calculated results is shown in Table II.

TABLE II

EFFECT OF PRESSURE ON THE BROMINE ELECTRODE IN THE SILVER BROMIDE CELL

Pressure, cm.	75.66	60.15	44.36	60.36	75.64
Temperature, °C.	456.6	457.2	458.7	458.7	458.7
E (obs.), volt	0.7985	0.7912	0.7814	0.7909	0.7980
E (calcd.), volt	.7985	.7912	.7812	.7909	.7980

In order to determine the volume changes involved in mixing molten silver bromide and lithium bromide, density determinations were made

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[2] Lorenz, "Die Elektrolyse geschmolzener Salze," Dritter Teil, p. 30, "Elektromotorische Kräfte," Knappe, Halle a.S., 1906.

upon a solution containing a half mole fraction of each. The method consisted of weighing a previously standardized quartz cylinder filled with tungsten, first in air and then at various temperatures while suspended in the solution. The measurements are shown in Table III.

TABLE III

DENSITY OF 0.5 MOLE FRACTION LiBr IN AgBr

Temp., °C.	517.4	527.6	533.4	545.6	550.0	555 2
Density	4.051	4.041	4.036	4.026	4.022 (extrapolated)	4.017

Using the density values for silver bromide obtained by Lorenz and Höchberg[3] and for lithium bromide obtained by Brunner,[4] we have shown the densities and molal volumes at 550° in Table IV. The change in volume upon mixing is thus seen to be very slight.

TABLE IV

DENSITIES AND MOLAL VOLUMES OF SILVER BROMIDE AND LITHIUM BROMIDE AND THEIR SOLUTION AT 550°

Composition	Density	Molal volume in cc.
AgBr	5.457	34.40
0.5 mole fraction LiBr in AgBr	4.022	34.15 (34.27 on basis of additivity)
LiBr	2.545	34.15

Discussion of Results

The data for this system have been treated in a manner similar to that described in the preceding paper on the lead bromide–lead chloride system. The results are given in Table V and $-\bar{F}_1$ plotted against log $(1/N_1)$ in curve A, Fig. 2, where N_1 is the mole fraction of silver bromide. If we attempt to calculate $\bar{F}_1$ from N_1 as before, we find that both assumption of no ionization and of complete ionization lead to the same result, $a_1 = N_1$. This gives curve B, Fig. 2, much higher than the observed.

TABLE V

ENERGY RELATIONS OF SILVER BROMIDE WHEN DILUTED WITH LITHIUM BROMIDE

N_1	1.0000	0.5937	0.4086	02548	0.1100
$dE/dT \times 10^6$ (volts/deg.)	−290	−248	−204	−170	−76
ΔS_1 (cal./deg.)	−6.69	−5.72	−4.71	−3.92	−1.75
$\bar{S}_1$ (cal./deg.)	0.00	0.97	1.98	2 77	4.94
500°, E (volt)	0.7865	0.8085	0.8202	0.8301	0.8686
500°, ΔF_1 (cal.)	−18150	−18660	−18930	−19150	−20040
500°, $\bar{F}_1$ (cal.)	0	−510	−780	−1000	−1890
500°, ΔH_1 (cal.)	−23320	−23080	−22570	−22180	−21400
500°, $\bar{H}_1$ (cal.)	0	+240	+750	+1140	+1920
500°, a_1	1.0000	0.7188	0.6030	0.5197	0.2916
500°, γ	1.000	1.211	1.477	2.040	2.651
550°, E (volt)	0.7720	0.7961	0.8100	0 8216	0.8648
550°, ΔF_1 (cal.)	−17810	−18370	−18690	−18960	−19950

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[3] Lorenz and Hochberg, *Z. Krist.*, 288 (1916).

[4] Brunner, J. Am. Ceram. *Soc.*, 350 (1904).

TABLE V (*Concluded*)

550°, $\bar{F}_1$ (cal.)	0	−560	−880	−1150	−2140
550°, a_1	1.0000	0.7119	0.5852	0.4969	0.2703
550°, γ	1.000	1.199	1.432	1.950	2.457
600°, E (volt)	0.7577	0.7836	0.7993	0.8128	0.8610
600°, ΔF_1 (cal.)	−17480	−18080	−18440	−18750	−19870
600°, $\bar{F}_1$ (cal.)	0	−600	−960	−1270	−2390
600°, a_1	1.0000	0.7088	0.5753	0.4808	0.2533
600°, γ	1.000	1.194	1.408	1.887	2.303

In other words, there is a strong positive deviation of the activity from Raoult's law, since a_1 is greater than N_1. It therefore seems that, as with the lead bromide–lead chloride system, the change in interionic forces due to substitution of the smaller lithium ion for the silver ion should be considered. This attempt we will again postpone for a future communication when investigations now in progress will permit a more general treatment.

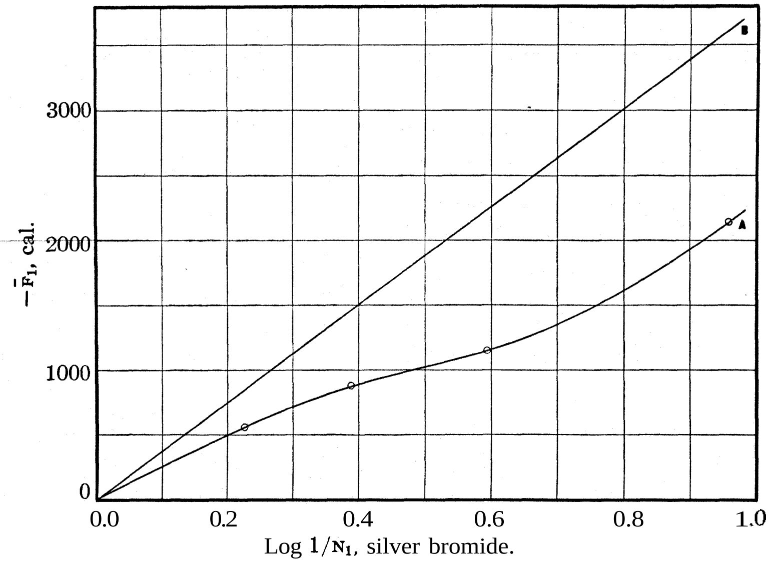

Fig. 2.—Change in free energy of silver bromide at 550° upon dilution with lithium bromide: A, observed; B, calculated.

Summary

1. The energy changes of molten silver bromide upon dilution with lithium bromide have been determined at mole fractions of lithium bromide varying from 0 to 0.89 between the temperatures of 450 to 600°.

2. The free energy of formation of pure molten silver bromide was found to be given by the equation $\Delta F_0 = -21{,}510 + 6.7\,t$ between 440 and 575°.

3. Density determinations of 0.6 mole fraction lithium bromide in silver bromide were made between 517 and 555° and may be expressed by the equation $d^t = 4.504 - 0.000877\ t$.

4. The results have been discussed on the basis of simple assumptions as to ionization, but without taking into account any changes in interionic forces upon dilution.

BERKELEY, CALIFORNIA

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

THERMODYNAMIC PROPERTIES OF SOLUTIONS OF MOLTEN LEAD CHLORIDE AND ZINC CHLORIDE

BY A. WACHTER AND J. H. HILDEBRAND

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The following investigation represents a contribution to the program begun by Hildebrand and Ruhle[1] of gathering data upon free energy of dilution of molten salt solutions. The system selected, solutions of lead and zinc chlorides, seemed to be simpler than many others, for the freezing point–composition diagram, obtained by Herrmann,[2] shows no evidence of solid compounds. As in the research of Hildebrand and Ruhle, we started with measurements of the e. m. f. of the cell Pb (liq.) | $PbCl_2$ (liq.) | Cl_2 (gas), but instead of producing the chlorine electrode by polarization, as in the earlier work, and as was done by Lorenz[3] and co-workers for a number of molten chlorides, we succeeded in getting a reversible chlorine electrode, reproducible over a range of pressure and temperature. The lead chloride was then diluted with zinc chloride and the free energy of the dilution determined from the change of e. m. f. of the cell, a procedure which avoids the uncertainty of a liquid junction.

A similar study of certain bromide systems by Salstrom and Hildebrand[4] was carried out approximately at the same time as this one, and the procedure was developed more or less in common. We will therefore avoid needless repetition by referring the reader to the description already given and state here only the features peculiar to this research.

The chlorine, the lead and zinc and their chlorides were from commercial sources of high purity, analyses of which were furnished, and were considered by us to be free from impurities that could affect the e. m. f. Substitution of chlorine generated by electrolysis of pure fused lead chloride made no appreciable difference in the results. The most serious im-

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[1] Hildebrand and Ruhle, THIS JOURNAL, 49, 722 (1927).

[2] Herrmann, *Z. anorg. Chem.*, 71, 281 (1911).

[3] Lorenz, "Die Elektrolyse geschmolzener Salze," Dritte Teil, Elektromotorische Kräfte, Knappe, Halle a. S., 1906; *Z. physik. Chem.*, 62, 119 (1908); 63, 109 (1908); *Z. angew. Chem.*, 39, 88 (1926).

[4] Salstrom and Hildebrand, THIS JOURNAL, 52, 4650 (1930).

purity to be avoided was water; hence not only was the chlorine carefully dried in a tower containing glass beads wet with sulfuric acid, but the lead and zinc chlorides were fused in dry hydrogen chloride gas before weighing and introduction into the cell, and the cell itself, after being made up, was treated with dry hydrogen chloride bubbled up through the molten salt for about an hour.

Reproducible values for the cells were reached after chlorine had been bubbled through them for from twelve to twenty-four hours. After that they responded very quickly to temperature changes with no evidence of hysteresis. The effect of changing the pressure of the chlorine was studied using five different pressures from 76 to 105 cm. The changes in e. m. f. so produced agreed within 0.3 millivolt with those calculated by aid of the usual formula. Electrolysis of the cells at 0.25 ampere for two hours caused no change in e. m. f., although a current of 3 amperes decreased the e. m. f. by several millivolts.

Since the theoretical treatment of our results will ultimately require a knowledge of the interionic distances, we considered it desirable to measure the densities of the two pure chlorides as well as their 50 molal per cent. solution. This was done by weighing a tungsten-weighted pyrex bulb in air, in water and in fused salt, correcting for the expansion of the bulb. The bulb was sharply tapped after each reading to remove any adherent bubbles of gas. The densities observed are given in Table I.

TABLE I

DENSITIES OF LIQUID LEAD AND ZINC CHLORIDES

100% $PbCl_2$		49.8% $PbCl_2$, 50.2% $ZnCl_2$		100% $ZnCl_2$	
t, °C.	Density	t, °C.	Density	t, °C.	Density
545.3	4.872	552.5	3.703	550.7	2.401
537.2	4.886	545.4	3.709	549.3	2.401
535.5	4.886	535.2	3.717	524.5	2.413
526.7	4.902	510.2	3.733	509.3	2.420
514.4	4.924			503.2	2.422
502.1	4.944			493.7	2.427
				485.7	2.431

The observed values yield the following equations: for the density of lead chloride: $d^t = 4.947 - 0.00164\ (t - 500)$; for the density of zinc chloride, $d^t = 2.424 - 0.00046\ (t - 500)$. Lorenz, Frei and Jabs,[5] using a platinum cube, obtained a density of 4.907 for pure lead chloride at 500°, differing from ours by 0.04 g. per cc. The molal volumes of lead and zinc chlorides at 500° are, respectively, 56.22 cc. and 55.82 cc., nearly identical. A 50 mole per cent. solution at this temperature has a molal volume of 55.31 cc., which is 0.7 cc. less than additive.

The results of the e. m. f. measurements are given in Table II and plotted in Fig. 1. The values for pure lead chloride represent three dif-

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[5] Lorenz, Frei and Jabs, *Z. physik. Chem.*, 61, 468 (1908).

TABLE II

E. M. F. IN VOLTS OF CELLS CONTAINING LEAD CHLORIDE OF VARIOUS MOLE FRACTIONS, N_1, DILUTED WITH ZINC CHLORIDE

t, °C. N_1 = 1.000	E. m. f.	t, °C. N_1 = 0.855	E. m. f.	t, °C. N_1 = 0.595	E. m. f.	t, °C. N_1 = 0.400	E. m. f.	t, °C. N_1 = 0.301	E. m. f.
499.1	1.2731	515.6	1.2703	493.4	1.3021	495.0	1.3125	494.7	1.3341
510.5	1.2653	520.7	1.2670	512.6	1.2921	504.8	1.3068	503.4	1.3296
517.5	1.2631	527.6	1.2629	534.4	1.2792	528.2	1.2933	512.3	1.3253
521.7	1.2603	531.3	1.2609	538.0	1.2770	537.9	1.2882	517.0	1.3224
525.3	1.2563	536.7	1.2574	545.3	1.2728	562.3	1.2738	525.0	1.3185
529.2	1.2554	540.6	1.2549	547.5	1.2713	567.4	1.2708	529.0	1.3162
536.8	1.2507	554.6	1.2461	557.9	1.2650	595.5	1.2540	541.3	1.3098
539.4	1.2488	587.0	1.2248	561.3	1.2636	602.2	1.2503	545.7	1.3079
541.8	1.2469			563.0	1.2617			579.1	1.2910
544.8	1.2445	N_1 = 0.688		568.2	1.2584				
549.5	1.2417	495.8	1.2934						
554.8	1.2394	512.7	1.2828						
556.5	1.2374	525.2	1.2753						
560.3	1.2350	542.5	1.2650						
566.0	1.2310	551.0	1.2602						
572.0	1.2281	560.0	1.2546						
578.5	1.2249	566.2	1.2510						
582.1	1.2221	570.0	1.2492						

ferent cells, indicated in the figure by points of different styles. No systematic differences between these cells could be detected. The points for each composition, although recorded in the table in order of increasing temperature, were not obtained in this order, but some were approached from above and some from below. The average deviation of our points from the straight line of the plot is less than 0.5 mv.

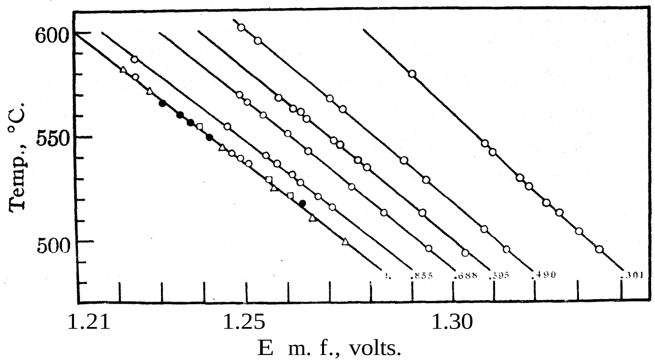

Fig. 1.—Temperature variation of e. m. f. of cells containing different mole fractions of lead chloride–zinc chloride solutions. Different symbols represent different cells at mole fraction 1.

In order to be sure that there was no danger of the lead electrode replacing zinc, we measured the e. m. f. of the cell Zn (liq.) | $ZnCl_2$ (liq.) | Cl_2.

The results are given in Table III. They show the e. m. f. to be sufficiently large to indicate that such displacement would not be a disturbing factor.

TABLE III

E. M. F. IN VOLTS OF THE CELL *Zn* (LIQ.) | $ZnCl_2$ (LIQ.) | Cl_2

t, °C.	501.0	504.1	518.7	527.8	531.4	541.0	550.2	565.2	575.5
E.m.f.	1.5721	1.5695	1.5593	1.5529	1.5498	1.5440	1.5369	1.5277	1.5199

Our results for the pure chlorides can be compared with those obtained by previous workers. Lorenz and Czepinski,[6] using a polarized electrode and taking no special precautions to exclude oxygen or moisture, obtained very fluctuating values, about 30 mv. less than ours for lead chloride and 60 mv. less for zinc chloride. Lorenz and Weber,[7] excluding air obtained values for lead chloride about 15 mv. less than ours, and Hildebrand and Ruhle,[1] taking proper precautions but using a polarized electrode, found values close to ours at 500° but falling off considerably at higher temperatures, 13 mv. at 600°. Recently Lorenz and Velde,[8] employing a procedure essentially the same as ours except that their preliminary treatment involved electrolysis of the cells for eight days at 0.25 ampere, obtained figures for lead chloride agreeing with ours to within 4 mv. For zinc chloride their values are 10 mv. less at 500° but in good agreement at 600°.

Since our main interest lies in the relation of free energy to composition at constant temperature, we obtained from Fig. 1, plotted on a large scale, the intersections at the round temperatures 500 and 600°, getting the values of e. m. f., E, given in Table IV, together with the values of dE/dT at the different compositions. The temperature coefficients fall off almost linearly with N_1 except for the most dilute cell, in which case it is considerably smaller. Since such a difference can hardly be real, it seems to us that the figures for this composition, $N_1 = 0.301$, are probably less accurate than the others.

Table IV also contains the values of the entropy, ΔS_1, and free energy of formation, ΔF_1, of lead chloride, its partial molal free energy or free energy of dilution, $\bar{F}_1$, its activity, a_1 and its activity coefficient, a_1/N_1. All of these have been calculated from the observed data by the usual formulas. We have also calculated the molal heat of formation, getting $\Delta H_1 = -81{,}100$ cal. for the pure liquid; this varies scarcely at all with changing temperature or upon dilution with zinc chloride.

The values for zinc chloride in Table III yield in a similar manner $E = 1.5725 - 0.000695(t - 500)$ for the e. m. f. between 500 and 600°, also, at 500°, $\Delta F_2 = -72{,}550$ cal. and $\Delta H_2 = -97{,}300$ cal.

[6] Lorenz and Czepinski, *Z. anorg. Chem.*, **19**, 208 (1899).

[7] Lorenz and Weber, *ibid.*, **21**, 305 (1899).

[8] Lorenz and Velde, *ibid.*, **183**, 90 (1929).

TABLE IV

THERMODYNAMIC PROPERTIES OF LEAD CHLORIDE DILUTED WITH ZINC CHLORIDE

N_1	1.000	**0.885**	0.688	0.595	0.490	0.301
dE/dT, mv./deg.	−0 625	−0.615	−0.595	−0.585	−0.575	−0.515
ΔS_1, cal./deg.	−28.9	−28.4	−27.5	−27.0	−26 6	−23.8
			500°			
E, volts	1 2730	1.2800	1.2905	1.2990	1.3095	1.3315
$-\Delta F_1$, cal.	58,750	59,050	59,550	59,950	60,450	61,450
$-\bar{F}_1$, cal.	0	300	800	1200	1700	2700
a_1	1.000	0.820	0.595	0.455	0.330	0.175
a_1/N_1	1 000	0 930	0 865	0.770	0.675	0.575
			600°			
E, volts	12105	1.2185	1.2310	1.2405	1.2520	1.2800
$-\Delta F_1$, cal.	55,850	56,200	56,800	57,250	57,750	59,050
$-\bar{F}_1$, cal.	0	350	950	1400	1900	3200
a_1	1.000	0.835	0.580	0.445	0.335	0.155
a_1/N_1	1.000	0.945	0.840	0.750	0.685	0.515

The general nature of the results is most clearly indicated by the values of a_1/N_1, which are less than unity in the solutions, corresponding to negative deviations from Raoult's law, as found by Salstrom and Hildebrand[4] for the solutions of lead chloride with lead bromide. We find in this case, however, that the simple assumption of complete ionization of both salts, with no change in interionic forces, does not account for the direction of the deviation. Since the dilution with zinc chloride would, if both salts were completely ionized, make no change in the proportion of chloride ion, the only effect would be due to the substitution of lead ion by zinc ion, reducing the activity of the former and hence of the lead chloride, in proportion to N_1, the same as for the case of no ionization.

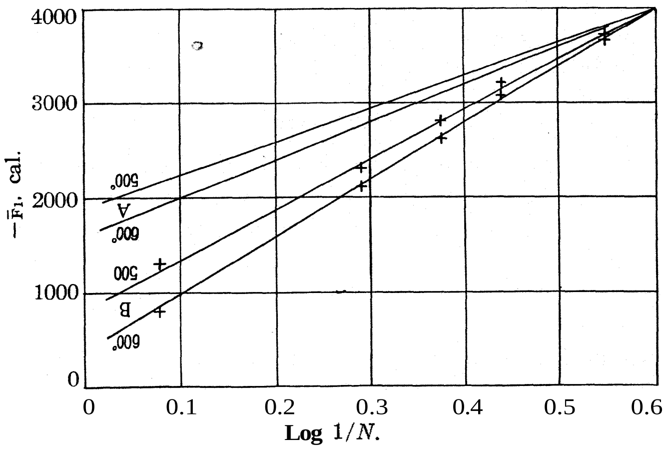

Fig. 2.—Variation of free energy of dilution with composition.

That a mere change in the interionic forces of a completely ionized mixture of these salts could affect the activities of the ions would seem plausible only in view of the contraction on mixing amounting to a little over one per cent., as shown by our density determinations. We will postpone till later any attempt to calculate the magnitude of this effect.

The deviation of the experimental results from the previous assumptions leading to $a_1 = N_1$ is illustrated graphically in Fig. 2, where $-\bar{F}_1$ is plotted against log $(1/N_1)$ for 500 and 600°. In view of the equation $\bar{F}_1 = RT \ln a_1$, this method of plotting yields the straight lines, A, when $a_1 = N_1$. As a matter of fact the empirical relation $\bar{F}_1 = 1.5\ RT \ln N_1$, given by the curves B, reproduces the experimental values very well.

An explanation of the deviations from $a_1 = N_1$ might be sought in a difference of dissociation between the two salts. Support for this view is lent by the fact that the electrical conductivity of zinc chloride at 500° is only one-sixteenth that of lead chloride, 0.084 mhos as compared with 1.33 mhos. Zinc chloride shows further evidence of low polarity in its low melting and boiling points and in its considerable solubility in various organic solvents. However, the most obvious difficulty in the way of an explanation along this line lies in the fact that we would not expect zinc chloride to have so much effect in small concentrations, but rather that curves B would begin tangent to curves A when N_1 is unity.

We will postpone a more searching treatment of this system till we have at hand data now being obtained for other systems, when we expect to make a comprehensive study of the whole subject.

Summary

1. The free energy of the formation of liquid lead and zinc chlorides has been measured between 500 and 600° by measuring the e. m. f. of reversible cells with metal and chlorine electrodes and fused salt electrolytes.

2. The e. m. f. of the Pb | $PbCl_2$ | Cl_2 in this range is given in volts by $1.2730 - 0.000625\ (t - 500)$, that of the corresponding zinc cell by $1.5725 - 0.000695\ (t - 500)$.

3. Dilution of the lead chloride by zinc chloride yields values for e. m. f. from which have been calculated the free energy of dilution and the activity over a range of composition from 30 to 100 mole per cent. of lead chloride.

4. It is pointed out that neither the assumption of no ionization or of complete ionization of both salts accounts for the observed values. Assuming the lead chloride to be ionized and the zinc chloride unionized accounts for the results only partially.

5. The densities of the pure salts and their 50 mole per cent. mixture have been measured in order to furnish information regarding interionic distances as a guide to a future theoretical treatment. The density of

lead chloride is given by 4.947 − 0.00164 (t − 500), that of zinc chloride by 2.424 − 0.00046 (t − 500).

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

AN ATTEMPT TO MEASURE THE VELOCITY OF DISSOCIATION OF NITROGEN TETROXIDE BY THE METHOD OF SOUND WAVES

BY GEORGE B. KISTIAKOWSKY AND WILLIAM T. RICHARDS

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For some years it has been apparent that sound waves offer an opportunity to investigate the velocity of dissociation of rapidly dissociating gases. The argument was at first[1] purely qualitative, it being supposed that when the compressions and rarefactions in the sound waves succeeded each other with sufficient rapidity the dissociating gas would no longer be able to attain equilibrium. An increased velocity of sound with increasing frequency was therefore to be expected when a certain critical region of frequency had been reached. Einstein gave this conception greater precision in a well-known paper[2] relating the velocity constant of the reaction to the increase in velocity of sound with increasing frequency. Since the velocity constants of rapid reactions are of the utmost importance for the kinetic interpretation of reaction velocities, Einstein's theory was soon tested, first by Selle[3] and later by Grüneisen and Goens.[4] Nitrogen tetroxide, which dissociates considerably in a convenient temperature range, was the object of study of both of these investigations. The work of Grüneisen and Goens was of an extremely scholarly character, the velocity of sound being measured by the resonance tube method to frequencies of 15,600 cycles per second from 10 to 35° and from 760 to 265 mm. pressure. The velocity being independent of frequency to a few tenths of a per cent. over this range, these authors estimated that the velocity constant of the reaction must exceed 10,000, a conclusion with which this communication is in entire accord. More recently Olson and Teeter[5] in a brief note, report an increase of velocity at 50 kilocycles. Their results have not been confirmed by this investigation. Their published data are limited, and no critique of their conclusion can be attempted here. It seems possible that they have underestimated their systematic error, a point of unusual importance in the calculation of the velocity constant.

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[1] Keutel, "Inaug. Disser.," Berlin, 1910.

[2] A. Einstein, *Sitzb. Berl. Akad.*, 380 (1920).

[3] H. Selle, *Z. physik. Chem.*, 104, 1 (1923).

[4] E. Grüneisen and E. Goens, *Ann. Physik.*, 72, 193 (1923).

[5] A. R. Olson and C. E. Teeter, *Nature*, 125, 150 (1930).

The discovery by Pierce[6] of the magneto-striction oscillator made easily available a far wider range of conditions, and suggested a reexamination of nitrogen tetroxide. The negative result obtained from this study was not to be expected, and leads to certain theoretical conclusions.

Experimental Procedure

The apparatus employed was necessarily rather complex, and in the interests of space conservation no attempt will be made to describe it completely. It naturally falls into two main divisions, the electrical circuit, which generated the sound waves, detected their nodal points in the gas-filled tube, and measured their frequencies, and the glass apparatus which generated and purified nitrogen tetroxide, maintained its temperature, and measured its pressure during the progress of the experiment. It will be convenient to describe the two separately.

The magneto-striction oscillators employed followed closely the design of Pierce[6] and drove one of three one-inch nichrome rods. The frequencies of these were approximately 10, 41.5 and 80 k. c. respectively. At the termination of an experiment with a given frequency the rod which had been used was heterodyned against another rod and the resulting beat note analyzed on a bridge closely resembling that recommended by Pierce. The variable inductance and capacity in this bridge were Leeds and Northrup calibrated precision instruments and gave the frequency of the heterodyne note to better than twenty cycles. Appropriate corrections for the temperature of the rods were, of course, applied. The rods were finally compared, by means of an intermediate heterodyne nichrome rod of about 45 k. c., with a calibrated quartz crystal of 47.45 k. c. (temperature coefficient 0.47 cycle per degree centigrade). The frequencies of the nichrome rods used during the experiments were therefore known with an estimated error of 20 cycles, or, respectively, 0.2, 0.05 and 0.03% for the 10, 41.5 and 80 k. c. rods. The greatest error in this determination was in the calibration of the capacities and inductance of the frequency bridge, and was largely eliminated by making many readings with a wide range of capacities and inductance and averaging. A characteristic series of such measurements follows.

TABLE I

TYPICAL FREQUENCY DIFFERENCES AS READ FROM CAPACITY BRIDGE

Difference in frequency in cycles per second between fourth harmonic of 10 k. c rod (at 25°) and 41.5 k. c. rod at 20.7°.

1987, 2021, 1978, 1987, 1984, 1953, Av. = 1985

Corr. to 25° = 1969

Of the glass apparatus only one piece, the observation tube, merits a detailed description. Since nitrogen tetroxide is a highly corrosive gas it was necessary that this tube be constructed as far as possible of materials exceedingly resistant to oxidizing action. Glass and nichrome satisfy this condition and, as a glance at Fig. 1 will show, no other materials were found necessary with the exception of a single small and well-protected cement joint. In Fig. 1, A represents the one-inch nichrome rod balanced on a

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[6] G. W. Pierce, Proc. *Am. Acad. Sci.*, **63**, 1 (1928). Mr. W. J. Cahill, whose work under Professor Pierce demonstrated the precision of measurements made with 2.54-cm. magnetostriction rods in 2.54-cm. tubes, acted as advisor in the very early stages of this investigation.

small asbestos support B, and fitting as tightly as possible without cramping its oscillations the long straight uniform glass tube which constituted the observation chamber. The driving coils for this rod were slipped over the outside of the tube, and were interchangeable with a magnetizing coil which made it possible to polarize the rod and change its position without opening the sealed tube at C. At the conclusion of any experiment the tube was blown open at C, another rod substituted for A, and the tube resealed, thus making a removable joint with possible leakage, oxidizable grease, etc., entirely unnecessary. The gas space through which sound waves were transmitted is represented by the region D. E is a piston of glass tubing which fitted snugly the main tube, and had a polished reflecting face carefully adjusted normal to the walls of the latter. Scrupulous plane-parallelism between this reflecting surface and the end of the nichrome rod is, of course, necessary to secure accurate measurements of the half-wave length of sound. The piston was sealed at F to two lengths of glass rod which extended parallel through the distance of motion of the piston, and terminated in a nichrome nut G which was sealed to them by glass-covered tungsten wires. A loop of glass-supported nichrome rod H shaped to receive the parallel glass rods served to prevent irregularities in the orientation of the polished piston face E by providing a rigid guide for the motion of the parallel glass rods. Motion of the piston was obtained by means of a nichrome screw which passed through G, and out of the tube through the asbestos–graphite packing I. A knurled handle, J, was rigidly attached to the screw. The side-tube K, which served to introduce the gas to be observed, is shown sealed as during the progress of an experiment. At L was a quartz spiral manometer which was attached to the apparatus throughout the experiments. and served to measure the pressures of gas in the tube to ±1 mm.

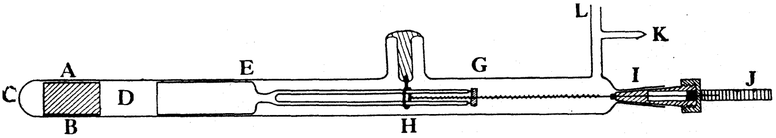

Fig. 1.—Glass chamber for measuring the velocity of sound in a corrosive gas.

Nitrogen tetroxide was prepared in the usual manner by heating lead nitrate in a stream of oxygen. The gas was repeatedly dried by passing through phosphoric anhydride tubes, and finally subjected to a vacuum distillation, being condensed at the temperature of solid carbon dioxide to rid it of any adsorbed or included permanent gases. It was then allowed to evaporate into the already evacuated apparatus and the purification, pumping, etc., systems were sealed off, leaving the apparatus essentially as illustrated in Fig. 1.

During an experiment the apparatus, with the exception of the quartz manometer, was covered with an air thermostat which maintained 25.0 ± 0.1°. The position of the piston was ascertained through a plate glass window by a cathetometer mounted scrupulously parallel to the axis of the piston. This gave complete independence of irregularities in the construction of the screw, and defined the position of the piston to 0.1 mm. The pressure and temperature of the gas were read at the start and finish of the experiments, and at such intermediate points as seemed advisable. Experiments with air were made with dry, carbon dioxide-free air. Experiments with nitrogen tetroxide were begun at atmospheric pressure, and the pressure progressively diminished by condensing out portions of the gas in small tubes at K (Fig. 1), which were then sealed off. This served the further useful purpose of indicating the presence of nitric oxide by the bluish color of the condensate, and of permanent gases by the slowness of the process of condensation. If either was found present in appreciable quantity the experiment was discontinued and the result discarded.

The half wave length of sound was determined as the difference between the position of the piston at two resonance points. The resonance points were determined by a milliammeter in the plate circuit of the amplifier of the oscillating circuit, the reflection of sound from the piston at the resonance point greatly increasing the plate current. By suitable adjustment almost any desired magnitude of deflection could be obtained. The resonance points were uniformly sharp and evenly spaced over the entire range of the piston stroke (some 200 mm.) at pressures down to 300 mm. At 140 mm. the enormous increase of absorption made it impossible to examine more than some twenty or thirty half wave lengths. Since the regularity of spacing of the resonance peaks is a matter of some importance for the interpretation of the results, one series of typical measurements on nitrogen tetroxide is given in Table II.

TABLE II

CATHETOMETER READINGS AND HALF WAVE LENGTH VALUES IN N_2O_4

41,633 cycles per second, 277 mm., and 25.0". Cathetometer readings made every 10 half wave lengths.

Mm.	670.1	646.6	623.3	599.9	576.5	553.1	529.6	506.1	482.6
Difference	23.5	23.3	23.4	23.4	23.4	23.5	23.5	23.5	

After condensing a portion of gas and re-evaporating, the last reading, 80 half wave lengths from first, was 482.7 mm. Velocity of sound $= 4.163 \times 10^4 (670.1 - 482.7) (2/80) = 195.2$ meters per sec.

Experimental Results

The results of all measurements may be summarized in a series of almost self-explanatory tables.

TABLE III

VELOCITY OF SOUND IN AIR AT 25.0° AND VARIOUS FREQUENCIES AND PRESSURES

Frequency	Pressure	Number of nodes	Velocity
9,916	730	8	345.6
41,633	758	40	346.5
41,633	152	40	346.5
80,350	760	110	345.5
80,350	147	20	346.1

In Table III, as in all subsequent tables, frequency is quoted in cycles per second, pressure in mm. of mercury, and velocity in meters per second. The number of nodes, or half-wave lengths, measured is also quoted, since this plays an obviously important part in estimating the relative accuracy of each particular measurement. The average value obtained from these figures is 346.0 meters per second and when reduced[7] to 0° becomes 331.2 meters per second, a satisfactory agreement with the most probable absolute value of 331.6 meters per second.

Tables IV, V and VI give similar data for nitrogen tetroxide at different frequencies, and, in addition, an arbitrary number which designates the sample of gas which filled the tube in each particular determination. The temperature coefficient, used for covering temperature variations of 0.1°,

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[7] The method of reduction and the next to most recent velocity of sound in dry air may be found in G. W. Pierce, *Proc. Am. Acad. Arts Sci.*, **60**, 281 (1925).

was taken from Grüneisen and Goens as 1.0 meter increase in velocity per degree centigrade at all pressures.

TABLE IV

VELOCITY OF SOUND IN N_2O_4 AT 9916 CYCLES PER SECOND, 25.0°, AND VARIOUS PRESSURES

Filling	Pressure	Number of nodes	Velocity
1	776	21	183.0
2	761	18	183.8
2	364	17	192.4
2	273	17	197.0
3	269	19	196.8

TABLE V

VELOCITY OF SOUND IN N_2O_4 AT 41,633 CYCLES PER SECOND. 25.0°, AND VARIOUS PRESSURES

Filling	Pressure	Number of nodes	Velocity
4	763	87	183.6
5	762	89	183.7
5	762	89	183.7
6	751	80	183.5
6	491	80	188.8
5	277	80	195.2
4	274	72	195.5
6	272	79	195.8
4	146	20	203.6
6	146	22	202.3

TABLE VI

VELOCITY OF SOUND IN N_2O_5 AT 80,350 CYCLES PER SECOND, 25.0°, AND VARIOUS PRESSURES

Filling	Pressure	Number of nodes	Velocity
7	765	110	183.6
8	764	150	182.5
7	759	140	184.2
9	759	55	184.0
10	754	150	184.1
11	752	100	184.0
11	752	160	183.9
7	487	110	189.4
7	485	109	189.4
12	333	128	193.5
7	304	193	195 3

The results given in Tables IV to VI have been represented as points in Fig. 2. The solid curve drawn through them defines the velocity of sound at all pressures considered to better than 0.5%, since the largest single deviation does not exceed this value. The figure demonstrates conclusively that, within this limit, there is no systematic change of velocity with frequency between 10 and 80 k. c., since the distribution of points about the solid curve appears perfectly random. It also should be noted that points measured by Griineisen and Goens show satisfactory agreement with the solid curve, especially since the pressure determinations for these points with the exception of the 760 mm. value depend on the vapor pressure data of nitrogen tetroxide[8] and hence may be considerably in error.

Several details call for brief comment. In the first place, it was most unfortunate that measurements could not be obtained at 140 mm. with the 80 k. c. oscillator, since this would have doubled the significance of the negative result reported. This was, of course, repeatedly attempted but, because of the difficulty of supporting adequately the very short rod for

[8] F. E. C. Scheffer and J. P. Treub, *Z. physik. Chem.*, 81, 308 (1912)

optimum oscillation conditions, because at such low pressures exceedingly little energy enters the gas from the vibrating metal, and because absorption was most pronounced, every attempt to measure velocities at this **frequency** below 300 mm. met with failure.

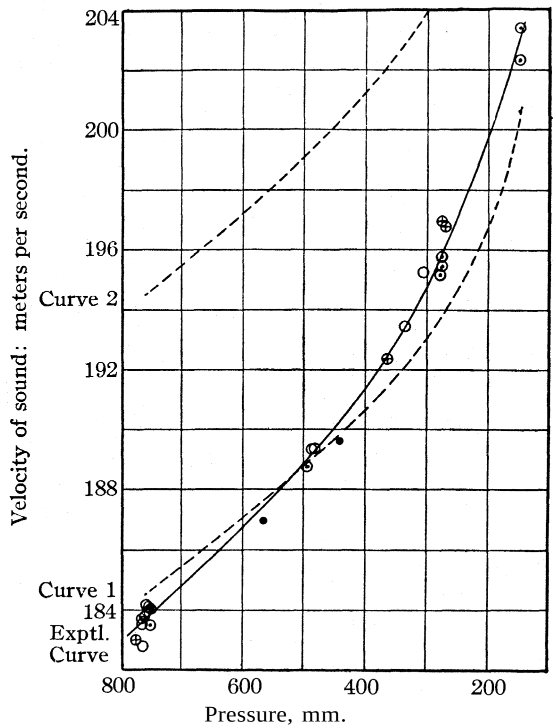

Fig. 2.—The velocity of sound in nitrogen tetroxide at 25° and various pressures: ⊕ represents 10 k. *c.* observations; ⊙, 41.5 k. c. observations; O, 80 k. *c.* observations, and ● the summarized observations of Grüneisen and Goens; Curve 1 represents the theoretical velocity according to Einstein for ω = o. Curve *2* for w = m.

Again, although the accuracy of any determination could have been increased by measuring a larger number of half-wave lengths, it was found unnecessary to do so. An examination of a relatively small number of nodes was sufficient to fix the velocity of sound in any particular determination to about 0.05% and errors in other parts of the procedure produced greater deviations than this. Each determination was carried out by running the piston along the tube from a position as near as possible to the vibrating rod to the end of its stroke, the spacing and number of the peaks being noted. A considerable quantity of the gas was then condensed out at K

(Fig. 1) and reëvaporated, and the peak nearest the end stroke of the piston redetermined. It was always found to check the previous value within 0.2 mm., which was the accuracy of determining a single resonance peak.

The greatest source of error was evidently small, almost undetectable traces of permament gases and nitric oxide, since variations of as much as 0.5% were observed between velocities measured with different fillings of the apparatus, No method of purification or evacuation was found completely to obviate these.

Theoretical Discussion

The Einstein theory permits the calculation of the velocity of sound in a dissociating gas at zero frequency, at infinite frequency and at intermediate frequency provided the absorption coefficient is sufficiently small. For zero frequency the expression is

$$V_{\omega = 0} = \sqrt{\frac{P}{\rho}\left(1 + \frac{A}{B}\right)} \tag{1}$$

for infinite frequency

$$V_{\omega = \infty} = \sqrt{\frac{P}{\rho}\left(1 + \frac{R}{\bar{c}_v}\right)} \tag{2}$$

and for intermediate frequencies

$$V_{\text{intermed.}} = \sqrt{\frac{P}{\rho}\left(1 + \frac{K^2AB + R\bar{c}_v\omega^2}{K^2B^2 + \bar{c}_v^2\omega^2}\right)} \tag{3}$$

where V represents the velocity of sound, ω the circular frequency, P the pressure, ρ the density, R the molecular gas constant, $\bar{c}_v$ the averaged specific heat at constant volume, K the velocity constant of dissociation, and A and B are abbreviation constants defined by

$$A = \left(2\frac{D}{T} - \bar{c}_v\right)\frac{n_1}{n_1 + n_2} + R\left(1 - 4\frac{n_1}{n_2}\right)$$

$$B = \frac{D^2}{RT^2}\frac{n_1}{n_1 + n_2} + \bar{c}_v\left(1 - 4\frac{n_1}{n_2}\right)$$

D being the heat of dissociation, T the temperature and n_1, n_2 the molecular numbers of nitrogen tetroxide and nitrogen dioxide, respectively.

For this calculation, therefore, a knowledge of the equilibrium constant of nitrogen tetroxide and its heat of dissociation, and of the specific heats of nitrogen dioxide and nitrogen tetroxide is necessary. The first two quantities were obtained from the work of Bodenstein,[9] the value of K being 0.1455 and of D 12,940 cal. at 25°. The specific heats of the gases have not been measured, and must be calculated on the basis of certain assumptions. It has therefore been assumed that c_v of nitrogen dioxide equals that of carbon dioxide, nitrous oxide, etc., namely, 6.8 cal., whereas that of nitrogen tetroxide is larger by 6/2 R calories, and hence becomes 12.75 cal. While no strong arguments for these values may be advanced,

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

they are reasonable approximations, and even if considerably in error the validity of the calculation would be little affected.

Using these values the pressure–velocity curves indicated by dotted lines 1 and 2 in Fig. 2 are obtained for Equations 1 and 2, respectively. It will be noted that dotted curve 2, which indicates the maximum effect possible, lies far above the observed values. Dotted curve 1 agrees better with the experiments here reported, but does not coincide within the limit of experimental error. This is not surprising, since the calculated velocity is highly sensitive to the values chosen for the dissociation data, as is strikingly illustrated by the fact that Grüneisen and Goens, using less accurate values for these quantities, obtain a calculated value for the velocity at 760 mm. which is almost 2% higher than that given on dotted curve 1.

Grüneisen and Goens, using Equation 3, and taking into account their probable experimental error, have estimated that at 25° the reaction velocity constant must be larger than 10^4. On the basis of the present communication this lower limit must be raised. It may safely be assumed that the probable error of the sound velocity measurements here reported does not exceed the maximum deviation, 0.5%, and hence the minimum velocity constants compatible with the 41.5 k. c. and 80 k. c. measurements are 2.6×10^4 and 5×10^4, respectively, since at these two frequencies agreement is obtained within the allowed error with determinations at lower frequencies.

It is of some interest to compare the lower limit of the velocity constant thus determined with the upper limit of the reaction velocity as deduced, on some assumption concerning the reaction mechanism, from the kinetic theory. It is most plausible to assume that the dissociation process belongs to the so-called "quasi-unimolecular" reaction type,[10] that, in other words, the activation of a nitrogen tetroxide molecule on collision is followed either by its decomposition or by its deactivation on another collision. Since, for the present purpose, only the upper limit of the reaction velocity is of interest, only the case need be considered where the mean life of the activated nitrogen tetroxide molecules is short compared with the time between inelastic collisions, and hence the rate of decomposition is essentially equal to the rate of activation. It will further be expedient to assign to the heat of activation its lowest possible value, the heat of reaction. Unfortunately, the cross sections of the nitrogen dioxide and nitrogen tetroxide molecules, which must be used to calculate the total number of kinetic collisions Z, are unknown and experimentally inaccessible. It is, therefore, necessary to assume cross sections for these molecules, and the values of $d_{NO_2} = d_{CO_2} = 4.2 \times 10^{-8}$ cm. and $d_{N_2O_4} = \sqrt[3]{2d^3_{NO_2}} = 5.3 \times 10^{-8}$ have been chosen as being least likely to be in error.

Granting these assumptions which, although not wholly defensible, can

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[10] Lindemann, *Trans. Faraday Soc.*, 17, 598 (1922).

hardly yield too low a value for the maximum dissociation velocity which is kinetically possible, the computation is easily made. The data employed may be either the measurements made at 150 mm. and 41.5 k. c. or 250 mm. and 80 k. c. since the result obtained will be approximately the same for the two. It follows from ordinary kinetic considerations that, if only two degrees of freedom of the molecule participate, the velocity of decomposition at 150 mm. and 25° will be

$$-\frac{dn_1}{dt} = Ze^{-D/RT} = 2.6 \times 10^{27} \times 2.7 \times 10^{-10} = 7 \times 10^{17} \text{ molecules per cc. per sec.}$$

t referring, of course, to time, and the other symbols having the significance defined above. From the minimum value of the velocity constant K determined by experiment at 41.5 k. c. and 150 mm. (2.6×10^4), it is evident that the rate of decomposition must be greater than $Kn_1 = 5.5 \times 10^{22}$ molecules per cc. per second, a number far greater than that calculated above. It is necessary, therefore, to assume, as has been done by Polanyi, Hinshelwood, and others for several reactions, that more than two degrees of freedom participate in the activation process. Since the total number of internal degrees of freedom of the nitrogen tetroxide molecule is twelve, the maximum possible rate of activation and reaction is given[11] approximately by

$$-\frac{dn_1}{dt} = Ze^{-D/RT}\frac{(D/RT)^{11}}{11!} = 1.1 \times 10^{25} \text{ moles per cc. per sec.}$$

this value is not greatly in excess of the experimental value, which indicates that the activation of nitrogen tetroxide must involve a large number of degrees of freedom, and hence be very similar in character to the decomposition of nitrogen pentoxide.

A comparison may also be made between the rate of association of nitrogen dioxide molecules—which, in the case under consideration, must be larger than 1.1×10^{23} molecules per cc. per sec.—and the number of triple collisions. The second quantity is easily estimated, using the approximation that the number of triple collisions is related to the number of all collisions as the molecular diameter to the mean free path, and may thus be assigned the value 2×10^{24}.

As a result of this calculation it may be stated with some confidence that the maximum theoretical velocity of decomposition and the number of triple collisions have values close to that calculated from the minimum velocity constant defined experimentally. The discrepancy between the two is sufficiently small to suggest at first sight the desirability of performing further measurements at higher frequencies and lower pressures in an attempt to discover whether or not the kinetic theory of reaction velocity may be applied to the process with ordinary molecular dimensions, or

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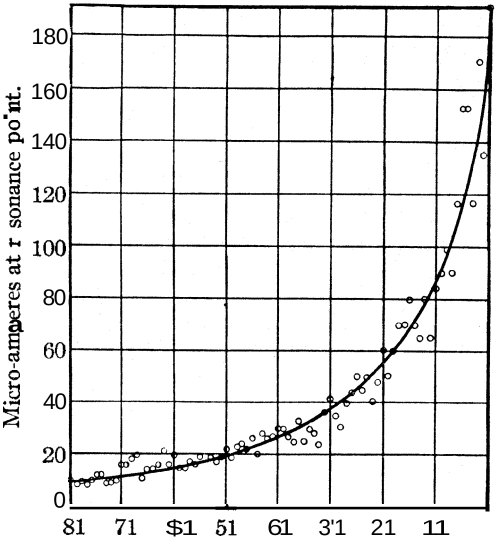
[11] K. F. Herzfeld "Kinetische Theorie der Wärme" Braunschweig. 1925.

whether larger effective cross sections must be postulated. More critically examined, such an extension of these measurements appears much less promising, owing to the greatly increased absorption of sound in nitrogen tetroxide at low pressures.

A few rough determinations of the absorption of sound were made in the course of the experimental work described above by noting the magnitude of change in plate current at succeeding nodal points. It cannot, of course, be claimed that this is a method of precision, but since no data of the kind have been published for nitrogen tetroxide, and since an assumption concerning absorption appears in the theory of Einstein, a brief summary of these observations will be set down here. Figure **3** represents a typical series of measurements, in this case those corresponding to the determination reported in detail in Table II. A line drawn through these points has a clearly exponential form, which may be expressed approximately by the empirical equation

$$I = I_0 e^{-hN}$$

where I and I_0 represent intensities, h an absorption coefficient and N the number of half wave lengths between I_0 and I. The values for h best fitting the curves at various pressures are given in Table VII.



Distance from rod in half wave lengths.

Fig. 3.—Absorption of sound in nitrogen tetroxide as illustrated by diminution in plate current at resonance points with increasing distance of reflector from vibrating rod. 41.5 k. c., 25.0°, 277 mm.

TABLE VII

ABSORPTION COEFFICIENTS IN NITROGEN TETROXIDE AT VARIOUS PRESSURES AND FREQUENCIES

Mm. pressure	760	400	150
10 k. c.	...	0.06	0.24
41.5 k. c.	0.02	.06	...
80 k. c.	.03	.05	0.20

It appears, therefore, that in nitrogen tetroxide the absorption of sound increases extremely rapidly below 400 mm. pressure, although, as is to be expected if the dissociation is far more rapid than the frequency, it is not noticeably dependent on frequency. similar measurements with air showed no significant change in h with pressure. The bearing of Table VII on further experiment is immediately apparent. Not only does the increased absorption at lower pressures very greatly diminish the accuracy of experiments by decreasing the number of half wave lengths which may be examined, but below 140 mm. the absorption becomes so great that it is likely that Einstein's reasoning would no longer apply. At increased frequencies it seems highly probable that absorption would set in at higher pressures, since Pierce[6] observed at 200 k. c. in carbon dioxide, a similar but non-dissociating gas, an absorption about a hundred times as great as that in air.

Measurements of this character are nevertheless being undertaken by one of us. It seems further advisable to investigate other dissociating gases and vapors in less accessible regions of temperature, for it is by no means certain that the behavior of nitrogen tetroxide is typical of all such dissociation processes.

Summary

1. The velocity of sound at 25° in nitrogen tetroxide has been investigated from 10 to 80 k. c., and from 760 to 140 mm., and has been found to be independent of frequency.
2. It has been calculated that the minimum velocity constant defined by these experiments is not far from the maximum possible velocity constant deduced from the kinetic theory of gases.
3. The bearing of this conclusion on the kinetic theory of reaction velocity is discussed.

PRINCETON, NEW JERSEY

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

PARAMAGNETISM INDEPENDENT OF THE TEMPERATURE AND THE EXISTENCE OF ELECTRONIC ISOMERS IN POLYATOMIC IONS

BY SIMON FREED AND CHARLES KASPER

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It has been almost universally believed that the phenomenon of paramagnetism owes its origin to the motion of the unbalanced electrons in the stationary states of molecules. Employing the model of such molecular magnets Langevin[1] was very successful in accounting for the magnetic behavior of many substances, not only in the gaseous state where interaction between the molecules is slight, but also in the crystalline state and in solution. He was led to Curie's law, which states that the paramagnetic susceptibility is inversely proportional to the absolute temperature. Many substances, however, display a somewhat more com-

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[1] Langevin, *Ann. chim. phys.*, [8] **5**, 70 (1905).

plicated behavior and require an arbitrary constant to describe their deviation from Curie's law.[2]

A number of substances have been found to have susceptibility quite independent of the temperature. Their paramagnetic susceptibility is small, usually of the same order of magnitude as the diamagnetic susceptibility. Indeed, such constant susceptibility may well be a general phenomenon experimentally inseparable from the diamagnetic susceptibility, since the latter is also independent of the temperature and in paramagnetic substances it may constitute part of the deviations from Curie's law. Only one type of substance exhibiting constant paramagnetism has been investigated here. It consists of a molecular ion in which a metallic constituent is surrounded with just the number of electrons which suggest a very balanced and symmetrical arrangement. One would, of course, expect such an ion to be diamagnetic. It was the aim in this investigation to observe by precise measurements to what degree the paramagnetism of such ions was independent of the temperature and to correlate their magnetism with the results of the quantum mechanics.

Previous **Work** and its Relation to the Present Investigation.—Manganese in permanganate ion, MnO_4^-, is in its maximum valence of +7, and it would normally be expected to resemble argon and be diamagnetic, since the latter has all its electrons mutually balanced.[3] Ishiwara[4] measured the specific susceptibility of potassium permanganate over a range of temperatures and found it to be 0.179 at 103°K., 0.175 at 294°K., 0.175 at 368°K. and 0.179 at 435°K.

Similarly, chromium in dichromate ion, $Cr_2O_7^{=}$, is in its maximum valence of +6. The susceptibility of this ion was found to be constant by Weiss and Collet[5] in solution from 14 to 50° within 1×10^{-6}, and by Collet[6] in the solid state from 12 to 90° to within 0.1×10^{-6}.

There are analogous ions such as UO_2^{++}, $WO_4^{=}$, VO_3^-, etc., which one would predict to behave similarly.

There is another type of ion manifesting constant paramagnetism,

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[2] A generalized Curie's law known as Weiss' law, $X(T + \Delta) = C$, is often obeyed; X is susceptibility, T, absolute temperature, Δ an empirical constant and C is Curie's constant.

[3] Kossel, *Ann. Physik*, 49,229 (1916), first observed that the paramagnetic susceptibility of many ions depends only on the number of unbalanced electrons in the valence shell. For example, bivalent vanadium, V^{++}, has three unbalanced electrons and it has three Bohr magnetons (Freed, THIS JOURNAL, 49, 2456 (1927)), VO^+ (V^{+++}) has two unbalanced electrons and it has two Bohr magnetons. VO^{++} (V^{++++}) has one unbalanced electron, as potassium has, and it possesses one Bohr magneton. VO_3^- (V^{5+}) has no unbalanced electrons, like argon, and hence would presumably be diamagnetic.

[4] Ishiwara, *Science Reports, Tôhoku Imp. Univ.*, Series I, **3**, **303** (1914).

[5] Weiss and Collet, *Compt. rend.*, 178, *2146* (1924).

[6] Collet, *ibid.*, 181, 1057 (1925).

which has some resemblance to the ions just mentioned, namely, the cobaltammines[6] and similar complex ions, and the ferrocyanide ion. The number of electrons surrounding cobalt in the cobaltammines is 36. The same number surrounds iron in ferrocyanide ion. Argon has the same number of electrons[7] and these, of course, balance completely and form a diamagnetic system.

Experimental Method

It was found that the method of Freed[8] for measuring susceptibilities at low temperatures would justify the use of a more sensitive balance than the one he employed. In the present work the apparatus was equipped with a Sartorius micro-balance having a capacity of 20 g. and a sensitivity under ideal conditions of ±0.001 mg. Under the conditions of the experimentation a sensitivity of about ±0.007 mg. was reached but the reproducibility was reduced to ±0.01 mg. or ±0.02 mg. by the fluctuations in the current exciting the magnet.

In short, the method consists in employing the use of the Gouy method at low temperatures in such a way that the tube containing the substance to be measured is in a regular stream of hydrogen at known temperatures. The hydrogen is cooled by liquid air, for example, boiling under atmospheric pressure, or to obtain lower temperatures, under reduced pressure. The stream of hydrogen gas is not connected with the vacuum pump and the tube swings just as freely at all temperatures as if it were suspended in air under atmospheric pressure. The balance can thus be manipulated as under normal conditions.

Materials and Experimental Results.—The chemical substances which were utilized in this work were analyzed for iron by the sensitive thiocyanate method and also for any other paramagnetic impurities that were likely to be present. Most careful attention was given to the possible presence of the metals of the ions in less than their maximum valence, for example U^{4+} in UO_2^{++}, Cr^{+++} in $Cr_2O_7^{=}$, etc. These are all paramagnetic and their undetected presence in appreciable concentration would have been disastrous. For this purpose, we observed colorimetrically the effect of adding permanganate solution drop by drop. This procedure was impossible in the case of dichromate due to its intense color. To avoid this, recrystallized potassium dichromate of great purity was measured magnetically and its susceptibility was found to increase slightly as the temperature was reduced. The same material was then recrystallized in the cold, that is by pumping off the water from a saturated solution at room temperature and distilling it into a liquid–air trap. The resulting dichromate crystals showed no temperature coefficient in the

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[7] Welo and Baudisch, *Nature*, 116, 606 (1925).

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

susceptibility. Perhaps it may be stated that the original paramagnetic contamination was so small that it would not have been detected by the previous investigators.

The susceptibility of uranyl ion decreased at first as the temperature was lowered, but increased again at lower temperatures. However, when the presence of iron was corrected for, the susceptibility continued to decrease steadily. If other undetected paramagnetic impurities had been present, the true susceptibility of UO_2^{++} would be decreasing more rapidly with decreasing temperature than appeared to be the case.

The sodium tungstate, $Na_2WO_4 \cdot 2H_2O$, was exceptionally free of impurities. It was recrystallized once.

The computation of the partial molal susceptibilities was made by assuming that the susceptibilities of the constituents were additive.

TABLE I

THE SUSCEPTIBILITIES OF UO_2^{++}

Temp., °K.	$\chi^a_{\text{gr. } UO_2SO_4 \cdot 3H_2O}$	$\chi^b_{\text{mole } UO_2^{++}}$
293.2	−0.0232	57.03
116.3	− .0212	56.28
90.8	− .0203	55.98
69.8	− .0228	53.97

[a] Uncorrected for ferric ion present. [b] Corrected for iron (2×10^{-6} g. per g. salt).

The second column is the susceptibility per gram of the salt $UO_2SO_4 \cdot 3H_2O$, which is effectually the difference between the susceptibilities of the paramagnetic and diamagnetic constituents. The partial molal susceptibility of UO_2^{++} can be ascertained with a greater percentage accuracy than this difference is known, provided the magnitudes of the diamagnetic susceptibilities are assumed to be without appreciable error. Such an assumption is justified, perhaps, in the case of liquid water. (The susceptibility of ice is a trifle less but is not known with the same accuracy.) 12.96×10^{-6} per mole was taken as its susceptibility. However, the molal susceptibility of $SO_4^{=}$ is only very approximate and should be redetermined. The value of -37.00×10^{-6} per mole was arbitrarily adopted for it. This value is correct to within about 3%. We cannot then insist upon the absolute magnitudes in the third column. The variation with the temperature is known with far greater accuracy than the values of the susceptibilities themselves. It was, of course, these variations with which this research was primarily concerned. The reproducibility in the measurements was such that a change in the susceptibility per gram of 0.0005×10^{-6} could be definitely established. Such a sensitivity corresponds to a change of 0.06×10^{-6} per mole.

Greater precision than this in terms of actual effects on the balance was obtained in the measurements of sodium tungstate. However, the pull was so great, about 10 mg. (it was only from 0.8 mg. to 1.7 mg. with $UO_2SO_4 \cdot 3H_2O$), that slight fluctuations in the current brought the reproducibility to ±0.02 mg. The susceptibility was measured at 296.5°K., 115.2°K. and 86.4°K. and was found to be constant. Of a total of thirty-six points only two deviated from the smooth curve of pulls against amperes by 0.03 mg. and one by 0.04 mg. The susceptibility per gram of the salt was found to be -0.1958×10^{-6} and the *susceptibility per mole of* $WO_4^=$ becomes $+5.93 \times 10^{-6}$. A change of 0.0005×10^{-6} per gram or 0.08×10^{-6} per mole would have been observed easily. The value of -10.4×10^{-6} was taken as the susceptibility of one mole of Na^+.[9]

Finer reproducibility was attained with $Cr_2O_7^=$. The purified potassium dichromate was measured at 293.6°K., 169.9°K., 114.0°K. and 84.3°K. and found to be constant. The measured values fell upon a smooth curve within ±0.01 mg. Of the thirty-six points only one deviated by more than this, and it deviated by 0.03 mg.

Another series of determinations was made to obtain the absolute susceptibility. It was suspected that the balance might have been jarred slightly since the previous calibration had been made. However, this series agreed with the first within 0.02 mg. The susceptibility per gram was found to be $+0.0962 \times 10^{-6}$. Employing the value of -16.9×10^{-6} as the molal susceptibility of K^+[9], the *susceptibility of one mole of* $Cr_2O_7^=$ *is* 62.1×10^{-6}. A change of 0.1×10^{-6} per mole would have been observable.

Discussion of Results

The existence of fluorescence from uranyl ion, UO_2^{++}, shows clearly the existence of an unusual freedom from interaction with external systems. Otherwise, the high density of matter in thermal agitation in the crystal would have quenched the fluorescence. The independence of the dichromate ions from one another is further confirmed in the identical susceptibility which dichromate ion has in solution and in the solid state. In the same way, the sharpness of the absorption bands of the permanganate ion, MnO_4^-,[10] indicates that its least stable electrons, that is, those to which one may assign the optical and paramagnetic properties of MnO_4^-, are shielded from external forces.

To a considerable degree of approximation, then, the least stable electrons of the ions we have been discussing may be regarded as localized near the metallic kernel of the ion and shielded from the external fields of the neighboring ions by the atmosphere of electronically saturated oxygen atoms (or ammonia, etc., in the cobaltammines or cyanide in the cyanides, etc.). Such a configuration immediately suggests the atomic

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[9] Ikenmeyer, *Ann. Physik*, [5] 1,169 (1929).

[10] Hagenbach and Percy. *Helv. Chim. Acta*, 5, 454 (1922).

ions of the rare earths whose kernels contain the unbalanced electrons. These, too, are shielded from external forces by electronically saturated shells, that is, by electronic shells which are completely filled.

The ions of the rare earths conform very closely in their magnetic behavior[11,8] with that expected from independent ions. Indeed, their magnetic susceptibilities can be calculated accurately from considerations employed in the quantum theory of atoms (atomic ions.) Correspondingly we shall attempt to correlate the magnetic properties of the molecular ions, such as UO_2^{++}, $WO_4^{=}$, $Cr_2O_7^{=}$, MnO_4^{-}, etc., with the quantum theory of molecules.

Van Vleck[12] in a series of important papers on susceptibility from the point of view of the quantum mechanics arrived at the following formula

$$\chi = \frac{N}{3kT}\,\frac{\Sigma_{\sigma jm,\,j'm'}\,|\,M(\sigma jm;\ \sigma j'm')\,|^2\,e^{-W(\sigma j)/kT}}{\Sigma_{\sigma jm}\,e^{-W(\sigma j)/kT}} \tag{1}$$

$$+\,\frac{--\cdot}{3h}\,\frac{\Sigma_{\sigma jm,\,\sigma'j'm'\,(\sigma \neq \sigma')}\,\frac{|\,M(\sigma jm;\ \sigma'j'm')\,|^2}{\nu(\sigma;\ \sigma')}\,e^{-W(\sigma j)/kT}}{\Sigma_{\sigma jm}\,e^{-W(\sigma j)/kT}} \tag{2}$$

$$-\,\frac{Ne^2}{6mc^2}\,\Sigma r^2 \tag{3}$$

where χ is the susceptibility per mole, k is Boltzmann's constant, T is the absolute temperature, σjm are indices or quantum numbers of the molecule in a stationary energy state, a is an index corresponding to quantum numbers whose change is associated with an energy W (a), large compared with kT (in the present case we may identify it with electronic quantum numbers), j corresponds to quantum numbers whose change implies energies small compared to kT (in this case the rotational quantum number, m, corresponds to quantum numbers whose change is associated with energies small compared with kT, in this case, magnetic quantum numbers), v (a; a') is the absorption frequency corresponding to a transition from the state a to a' (it is practically equal to v $(\sigma jm;\ j'm'$—, since the change in a is associated with a greater energy difference than is brought about by the change in the other quantum numbers), e/m is the charge divided by the mass of the electron, N is Avogadro's number, h is Planck's constant, c is the velocity of light and Σr^2 is the average of the square of the radii of the electronic orbits summed over all the electrons.

$|\,M(\sigma jm;\ \sigma j'm')\,|^2$ is the square of the absolute magnitude of the magnetic moment generated by the electrons in the stationary electronic state of the molecule. (If the molecule is symmetrical as one would believe MnO_4^{-}, UO_2^{++} to be, an axis of symmetry exists with respect to which the angular momentum of the system may be resolved. $\Sigma_{j'm}\,|\,M(\sigma jm;$

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[11] Hund, Z. *Physik*, 33,855 (1926).

[12] Van Vleck, (a) *Phys. Rev.*, 29,727 *(1927);* (b) 30, 31 (1927); (c) 31, 587 (1928).

$\sigma j'm')\,|^2$ can be visualized as the square of the magnetic moment parallel to this axis and $\Sigma\sigma j'm'(\sigma \neq \sigma')\ |\,M(\sigma jm;\ \sigma'j'm')\,|^2$ as the square of the magnetic moment perpendicular to this axis.) $\Sigma\sigma'j'm'(\sigma \neq \sigma')\ |\,M(\sigma jm;\ \sigma'j'm')\,|^2$ is the square of a sort of average magnetic moment associated with the transition $\nu(\sigma;\ \sigma')$.

$M(\sigma jm;\ \sigma'j'm')$ can be identified according to Van Vleck[13] and others as resulting from the fluctuation in angular momentum between the nuclei and the electrons. On the average the angular momentum in a stationary state of such ions as UO_2^{++} and $WO_4^{=}$ (doubtless having $^1\Sigma$ levels for their basic electronic states) is zero but instantaneously the square of the angular momentum (or magnetic moment) is not zero. The susceptibility arising from the magnetic moments of the stationary states would naturally be affected by the thermal agitation which counteracts the alignment induced by the magnetic field. Hence its susceptibility would show a dependence upon the temperature. The moment associated with a fluctuation which occurs with the frequency $\nu(\sigma;\ \sigma')$, which is very rapid as compared with thermal collisions, would of course not reflect its effect on the susceptibility as a function of the temperature. In line (2) we do not find T as a factor in the denominator. The Boltzmann factor contains the temperature, but its influence is inappreciable when the frequency is high. This term then becomes practically a constant. In fact, Van Vleck shows that when energy changes associated with j and m are small compared to energy changes associated with a, then form (2) reduces to

$$\frac{2N}{3h}\Sigma\sigma(\sigma \neq \sigma')\,\frac{|\,M(\sigma;\ \sigma')\,|^2}{v(\sigma;\ \sigma')} \tag{2a}$$

which is independent of the temperature. Line (3) comprises the diamagnetic contributions to the susceptibility. This results, of course, from the moment induced by the magnetic field and is not present in its absence.

As we have observed in the introduction, the ions we have been discussing have their net electronic moments equal to zero and hence would normally be diamagnetic. The first term in the summation on line (1) is then zero. Since the measured susceptibilities are practically independent of the temperature, the other terms of this summation are small, not because the moments in the activated states are zero (such a possibility is only very slight), but because the number present in those states is small. This number is, of course, regulated by the Boltzmann factor, which is small when the energy of activation, the frequency of transition, is large. The form of the term shows that the contribution of these activated molecules to the susceptibility would tend to have but a small temperature coefficient over a restricted temperature range. For example, the number present in the activated states increases with the tem-

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[13] Ref. 12c. p. 606.

perature, but on the other hand their susceptibility decreases. The bulk of the constant susceptibility arises from the second line, the so-called fluctuation term.

Since neither the frequency of transition in these ions nor the magnetic moments in their activated states are yet known, we must speak only in more or less qualitative terms. The results show that UO_2^{++} becomes less paramagnetic as the temperature is reduced (any paramagnetic impurity would introduce an opposite trend). The small variation over so considerable a temperature range indicates that the fluctuation term is the predominant one, that the electronic frequency probably lies in the infra-red and that the number in the activated level increases more than linearly with the temperature.

The constancy in the paramagnetism of $WO_4^=$ implies that the frequency of transition to the first electronic level (possessing a magnetic moment) is probably higher than that of UO_2^{++}. It follows that the contribution of the "parallel" (or temperature) component is small and also that the fluctuation term is small since the same high frequency occurs in its denominator. The actual magnitude of the susceptibility of $WO_4^=$ is really small. $WO_4^=$ is colorless and it is conceivable that the first electronic activation lies in the ultraviolet. Indeed, it may possibly lie in the continuum of dissociation.

$Cr_2O_7^=$ also possesses a paramagnetism independent of the temperature. The same reasoning applies to dichromate as to tungstate. If the first electronic activation corresponds to light in the visible, the frequency would be more than high enough to account for the lack of a temperature coefficient in its susceptibility.

MnO_4^- measured by Ishiwara[4] is the only ion of this type other than UO_2^{++} whose susceptibility is known to decrease with the temperature. At the lowest temperature, however, he found it to increase again. This is exactly the same behavior that UO_2^{++} apparently followed before its susceptibility was corrected for the presence of ferric ion. It appears very probable indeed that Ishiwara's potassium permanganate was slightly decomposed (by light, perhaps, or by some contact with organic matter, to which potassium permanganate is extremely sensitive), and as a result the paramagnetic manganese dioxide is present. Even a minute contamination becomes significant at the lower temperatures as its susceptibility is constantly increasing. If this slight impurity be discounted, the conclusion is reached that the susceptibility of MnO_4^- decreases steadily with the temperature just as UO_2^{++} was found to do, and the influences discussed in the case of UO_2^{++} apply here also.

In this discussion it has been assumed that the frequency $\nu(\sigma;\ \sigma')$ in the denominator of the fluctuation term does not vary with the temperature. This constancy is definitely not fulfilled in solids, as variations have been observed in the line spectra of the rare earths.[14] However, the magnitude of the change is small. The fact that both $WO_4^=$ and $Cr_2O_7^=$ display a susceptibility independent of the temperature indicates that the influence in ions of this nature is inappreciable.

Summary

The degree of dependence of the susceptibilities of UO_2^{++}, $WO_4^=$ and $Cr_2O_7^=$ on the temperature has been accurately studied from room temperature to that of liquid air.

The susceptibility of UO_2^{++} was found to decrease slightly and uniformly as the temperature was reduced. It is pointed out from the work of Ishiwara[4] that MnO_4^- behaves very probably in the same way.

$WO_4^=$ and $Cr_2O_7^=$ showed no variation in their susceptibilities within the experimental error. The latter ranged from 0.06×10^{-6} to 0.1×10^{-6} per mole or about 0.0005×10^{-6} per gram.

Various properties of these ions are taken as evidence that the ions are of such a nature as to permit the application of the modern theories of magnetism.

The constant paramagnetism of these ions[15] is related to the results of Van Vleck derived from the quantum mechanics. As a consequence, the existence of electronic isomers in these molecular (polyatomic) ions is recognized.

From this point of view, constant paramagnetism is a general phenomenon and is associated with the existence of activated electronic energy levels in molecules (or their ions) in the solid state and in solution as well as in the gaseous state.

BERKELEY, CALIFORNIA

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[14] Freed and Spedding, Phys. Rev., 34, 945 (1929).

[15] It is very probable that the constant paramagnetism exhibited by some solids cannot be approached in this manner. Their molecules cannot be regarded as isolated with sufficient approximation, and interactions characteristic of the crystal come into play. Magnetic oxides like CuO probably would be in this category. One would scarcely expect their partial molal susceptibility in solution in some diamagnetic medium to have the same value as in the pure solid. Such an identity in the susceptibilities actually exists among the ions we are studying. The constant paramagnetism exhibited by metals seems to have found a satisfactory explanation on the assumption of an electron gas in the metal obeying the Fermi–Dirac statistics; Pauli, *Z. Physik*, **41**, 81 (1927).

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THE VAPOR PRESSURES OF SELENIUM TETRACHLORIDE. THE EXISTENCE OF SELENIUM DICHLORIDE

BY DON M. YOST AND CHARLES E. KIRCHER

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Introduction

The former studies of the physical properties of selenium tetrachloride have been restricted to vapor density measurements and to the determination of its heat of formation from the elements. There is considerable lack of agreement between the results of the measurements of the vapor density made by different investigators, although in all cases the evidence for dissociation is fairly conclusive. Ramsay and Evans,[1] as a result of measurements by the method of Victor Meyer, give the degree of dissociation as zero at 200°, 0.19 at 210°, and 0.65 at 350°, while Clausnizer[2] finds complete dissociation at the temperature (not given) at which he worked, the vapor density being just one-half that calculated from the formula $SeCl_4$.

The recently published results of the very interesting experiments made by Simons[3] show definitely that the vapor density of selenium tetrachloride is one-half that to be expected from the formula over the temperature range from 200 to 600° and at atmospheric pressure.

The present investigation was undertaken to determine the extent and nature of this reported dissociation.

Experimental Method and Procedure

Owing to the corrosive action of selenium tetrachloride it was necessary to carry out the necessary pressure measurements in an all-glass apparatus. For this purpose the substance was placed in a cylindrical pyrex bulb at one end of which was sealed a so-called click-gage[4] also of pyrex. The gage was enclosed in and sealed to another glass tube, the latter being connected to the barometer used for measuring the pressures necessary to cause the gage to click. The whole assembly, reaction bulb and gage, being of one piece was placed in an electric furnace. The furnace was equipped with a copper core and auxiliary end coils for maintaining a

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[1] Ramsay and Evans, *J. Chem. Soc.*, 45, 62 (1884).

[2] Clausnizer, *Liebig's Ann. Chem.*, 196, 265 (1879).

[3] Simons, THIS JOURNAL, 52, 3483 (1930). This article appeared after the present work was completed. The present results, in so far as they are concerned with the vapor density, are in complete agreement with those of Simons. The temperature range over which selenium dichloride exists is shown by our results to be different than that suggested by him, his conclusions being based solely on observations of color changes.

[4] Daniels, Mathews and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, 1929.

uniform temperature in the central region and a slightly higher one at the end near which the bulb of the gage rested. It was thus possible to maintain the temperature of the reaction bulb constant, while that of the gage was kept slightly higher to prevent any condensation of solid material on it.

The temperature range investigated lay between room temperature and 230°. It was accordingly necessary first to investigate the characteristics of pyrex click-gages over this range. Small but definite changes in the pressure differences necessary to cause clicking were found at the higher temperatures, and, in fact, some gages ceased to operate after having reached the highest temperature. The gage eventually used suffered no great changes in its click constants even after repeated heating and cooling, the variations amounting on the average to about 2 mm. of mercury.

In making the measurements the temperature of the furnace was raised or lowered to some definite value and held there until the pressure remained constant. That equilibrium had been reached was established by varying the temperature above and below the selected one until the pressure changes responded to such variations. Equilibrium was approached from temperatures considerably above and below those at which measurements were made.

For the purpose of making vapor-density measurements the initial quantity of solid selenium tetrachloride taken was such that at the higher temperatures it would be completely vaporized. Moreover, after complete vaporization, the manner in which the pressures increased with increase in temperature was observed in order to determine the extent of any dissociation of the vapor itself. Thus it was found possible to make measurements of the vapor pressures, the vapor density and the degree of dissociation by a rather simple experimental device.

The accidental errors involved in the values given for the pressures consist of those arising from measurements of the temperature and pressure and do not exceed 3%. The absolute errors due to small losses of selenium tetrachloride during preparation, changes in the volume of the bulb and gage as a result of sealing it, and to the already mentioned variations of the click constant of the gage, do not exceed 2%, and most of this is to be ascribed to the two former causes. The accuracy of the vapor pressure measurements is probably greater than that of the vapor density.

Preparation of Materials

Great care was taken in the preparation of the selenium tetrachloride. The selenium itself was first purified by dissolving the C. P. material in concentrated nitric acid, filtering, evaporating almost to dryness, dissolving in concentrated hydrochloric acid and then precipitating with sulfur dioxide. The precipitate was washed repeatedly with cold water, and then with boiling water. This process[6] yields selenium free from

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[6] A. A. Noyes and W. C. Bray, "Qualitative Analysis for the Rare Elements," The Macmillan Company, New York, 1927, p. 381; Keller, THIS JOURNAL, 19, 771 (1897).

tellurium and was applied twice. The material so obtained was again dissolved in concentrated nitric acid, the solution evaporated almost to dryness, diluted to 400 cc. with water, filtered, and then treated with hydrazine hydrochloride. The resulting precipitate was thoroughly washed as before and finally dried and melted, and the melt poured into cold water in such a way that small spheres with diameters of 2 mm. and smaller were formed. This material was then dried.

To prepare the tetrachloride a weighed amount (about 0.0200 g.) of selenium was placed in a small glass tube one end of which was drawn down to a long thin capillary. the other end being then sealed to a drying tube containing anhydrous barium perchlorate. After displacing the air with carbon dioxide, chlorine was passed through the apparatus for some time, the vigor of the resulting reaction being diminished at the beginning by cooling the tube with a small lump of ice. When the reaction was almost complete it was necessary to heat the tube gently with the flame of a match in order to obtain complete conversion. Following this treatment the excess of chlorine was displaced with carbon dioxide. The tip of the capillary was then sealed, the whole assembly evacuated, and finally the tube containing the selenium tetrachloride sealed off. The material was almost white and was free from the lower chlorides. The tube containing the final product was placed in the reaction bulb, the bulb and gage were thoroughly evacuated, heat being applied to the bulb to drive out any adsorbed water, and finally the reaction bulb was sealed. The tube containing the tetrachloride was broken by shaking the reaction bulb.

The vapor of selenium tetrachloride has an intense orange color and at pressures of about one-fifth atmosphere a few diffuse absorption bands in the green region were observed.

For the experiments in which an excess of chlorine was present the procedure was as follows. A weighed amount of selenium in a small evacuated tube was placed in the reaction bulb and the latter carefully dried by heating and passing a stream of dried air through it. Dried chlorine was next passed through the bulb until the air had been swept out, after which the bulb was closed by sealing it, and the tube containing the selenium broken as before. The chlorine remaining was that in excess of the amount necessary to convert the selenium to the tetrachloride and was determined in advance by the amount of selenium taken.

Experimental Results and Discussion

TABLE I

VAPOR PRESSURES OF SOLID SELENIUM TETRACHLORIDE

Temperature, °C.	Pressure, mm.	Temperature, °C.	Pressure, mm.
109	11.3	157	157.8
120	23.9	161	203.4
129.5	40.0	163.6	235.8
131	42.6	170.5	310.6
140	65.5	171	317.7
149	111.1	175.5	389.6
150	117.4	180.5	482.0

In Table I are presented the final values for the vapor pressures of selenium tetrachloride. In Table II are given the values of the pressures after all the solid had been converted to the vapor, together with the pressures calculated on the assumption that the vapor consists of $SeCl_4$. All pressures are expressed in millimeters of mercury.

TABLE II

RESULTS OF PRESSURE–TEMPERATURE' EXPERIMENTS ON THE VAPOR FROM SELENIUM TETRACHLORIDE

Volume of reaction bulb and gage, 27.3 cc.
Wt. of selenium taken to prepare $SeCl_4$, 0.0188 g.
Wt. of Se calculated from gas law, assuming complete dissociation, 0.0185 g.
Wt. of Se calculated from slope of P–T curve, assuming complete dissociation, 0.0188 g.

Temp., °C.	Press. (obsd.), mm.	Pressure (calcd.) for normal $SeCl_4$ vapor, mm.	Ratio of obsd. to calcd. press.
189.2	489.6	250.7	1.95
191.5	495.3	251.9	1.97
199	502.2	256.0	1.96
199.5	502.6	256.2	1.96
208	612.1	260.9	1.96
209.5	513.4	261.7	1.96
215	520.1	264.7	1.96
223	526.6	269.0	1.96
226	533.5	270.6	1.96

The observed pressures given in Table II are, within the limits of the experimental errors involved, twice those calculated on the assumption that the vapor consists of $SeCl_4$. Moreover, the vapor obeys the simple gas law over the range where no solid is present. It may be concluded, therefore, that the selenium tetrachloride is, at these temperatures, completely dissociated in such a way that one molecule of it gives rise to two.

The vapor pressures of the solid increase very rapidly with the temperature. It was found that over the range of temperatures where the solid phase was present, the graph of $\log_{10}P_0$ plotted against the reciprocal of the absolute temperatures was a straight line. This fact indicates that the tetrachloride vapor is completely dissociated even at the lowest temperatures investigated.

There are three possible reactions that would be in accord with the results found experimentally, *viz.*

$$SeCl_4\ (s) = Se\ (s) + 2Cl_2\ (g) \tag{1}$$
$$2SeCl_4\ (s) = Se_2Cl_2\ (g) + 3Cl_2\ (g) \tag{2}$$
$$SeCl_4\ (s) = SeCl_2\ (g) + Cl_2\ (g) \tag{3}$$

Inasmuch as no solid or molten selenium (m. p. 217°) could be observed either in the vapor pressure experiments or in separate experiments devised to determine whether it were ever present, it is concluded that Reaction 1 does not occur.

If Reaction 2 or 3 takes place, chlorine should have a marked effect upon the vapor pressure of the solid. This was found by experiment to be the case. Indeed, it was found possible to establish that Reaction 3 is the correct one. If P_0 is the vapor pressure of the solid at a given temperature in the absence of excess of chlorine, and if complete dissociation takes place, then the equilibrium constants for Reactions 2 and 3 at the temperature in question are given by

$$K = \frac{27}{256} P_0^4 \quad (4) \qquad \text{and} \qquad K = \frac{1}{4} P_0^2 \qquad (5)$$

If excess of chlorine is present at the pressure p and if the total pressure is p_0, then for Reactions 2 and 3, respectively

$$P_0^4 = \frac{1}{27}(p_0 - p)(3p_0 + p)^3 \qquad (6)$$

$$P_0^2 = (p_0 - p)(p_0 + p) \qquad (7)$$

Applying Equations 6 and 7 to the results of the experiments in which excess of chlorine is present, the vapor pressure of the solid in the absence of excess of chlorine may be calculated. In Table III are given the results of such experiments together with the calculated and observed values of P_0. All pressures are expressed in mm. of mercury.

TABLE III

RESULTS OF EXPERIMENTS ON THE EFFECT OF CHLORINE ON THE VAPOR PRESSURE OF SELENIUM TETRACHLORIDE

Temp., °C.	Total press., mm.	Press. excess chlorine, mm.	P_0 (obs.) of $SeCl_4$, mm.	P_0 (calcd.) Eq. 7, mm.	P_0 (calcd.) Eq. 6, mm.
146	365.5	346.0	95.9	117.8	215.8
151	374.6	350.0	123.2	133.5	232.4
156	395.7	354.0	157.4	176.8	274.2
161	413.9	358.0	203.4	207.9	303.4
166	449.7	362.0	252.4	267.3	357.6
171	489.0	366.0	317.7	324.3	409.3
176	548.9	370.0	396.5	405 6	483.0

The results show that chlorine does have an effect on the vapor pressure of the tetrachloride, and that its magnitude corresponds to that demanded by Reaction 3, as may be seen by comparing the last three columns of Table III. It is, therefore, concluded that over the range of temperatures investigated the vapor phase consists of selenium dichloride and chlorine.

Thermochemical Results

The vapor pressures of selenium tetrachloride in equilibrium with the solid may be represented by the following formula[6]

$$\log_{10} P = -\frac{0.05223 \times 73{,}990}{T} + 11.2040$$

where P is expressed in millimeters of mercury and T is the absolute temperature.

The value of the heat of Reaction 3 is then

$$SeCl_4\,(s) = SeCl_2\,(g) + Cl_2\,(g) \quad \Delta H = 35{,}380 \text{ cal.}$$

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[6] The formula is set up so as to conform with the usage adopted by the "International Critical Tables."

Thomsen[7] gives the heat of formation of selenium tetrachloride as 46,156 cal. Combining this with the above we find

$$Se\ (s) + Cl_2\ (g) = SeCl_2\ (g) \quad \Delta H = -10{,}780\ \text{cal.}$$

It may be remarked that, if Reaction 1 or 2 be assumed as true, the calculated values for the heats of formation of $SeCl_4$ or Se_2Cl_2 differ greatly from the experimentally found values of Thomsen.

Stability of Selenium Dichloride

Attempts made heretofore to prepare selenium dichloride from equivalent amounts of the two elements have always met with failure, the resulting product consisting of a mixture of the solid tetrachloride and liquid monochloride. In analogy with sulfur and tellurium, the dichloride of selenium would be expected to exist, and its tendency to decompose with the formation of the tetrachloride and monochloride under normal conditions has doubtless prevented its previous detection. From the results of the investigation described in this paper the vapor form appears to be fairly stable. It is also possible that the vapor above liquid selenium monochloride consists, in part, at least, of the dichloride, since a considerable residue of elementary selenium always results after distillation. Moreover, the reported vapor density measurements on the monochloride show that there is no increase in the number of molecules on evaporation, even though a residue of elementary selenium is left behind. These facts would be in agreement with the assumption that the vapor consists of the dichloride.

Summary

The vapor pressures of selenium tetrachloride have been measured both in the presence and absence of excess of chlorine. From these results and the results of vapor density measurements it has been shown that over the range of temperatures from 109 to 226° the vapor consists entirely of selenium dichloride and chlorine.

The vapor pressures of the solid may be computed from the following formula where P is expressed in millimeters of mercury and T is the absolute temperature.

$$\log_{10} P = -\frac{0.05223 \times 73.990}{T} + 11.2040$$

The heat change accompanying the decomposition of solid selenium tetrachloride into the gaseous dichloride and chlorine is $\Delta H = 35{,}380$ cal. The heat of formation of gaseous selenium dichloride was found to be $\Delta H = -10{,}780$ cal.

PASADENA, CALIFORNIA

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[7] J. Thomsen, "Thermochem. Untersuchungen," Leipzig, 1882–1886; Abegg, Auerbach and Köppel, "Handbuch der anorg. Chem.," Leipzig, 1927, IV B, Abt. I, p. 723.

[CONTRIBUTION FROM PWSIKALISCH-CHEMISCHES INSTITUT DER TECHNISCHEN HOCHSCHULE, BRESLAU]

I. THE SPECIFIC HEATS OF THALLIUM, CALCIUM AND MAGNESIUM MEASURED TO 10° ABSOLUTE

II. THE ENTROPY AND CHEMICAL CONSTANTS OF MAGNESIUM FROM SPECTROSCOPIC DATA

BY K. CLUSIUS AND J. V. VAUGHEN

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This paper presents the results of the measurement of specific heats from 10 to 200° absolute, of thallium, calcium and magnesium. The specific heats of these metals have indeed been measured in the low-temperature range, yet in no case have they been measured to a sufficiently low temperature to permit a safe extrapolation to the absolute zero, which is necessary in the calculation of the entropy. Because of the peculiarity of the entropy function, the chief interest in these measurements has been in the region under 80°A. The apparatus, however, was capable of rendering exact results even at a temperature as high as 250°A.

Of special interest is a comparison between the entropy values obtained from calorimetric and from spectroscopic data, respectively. In order to make such a comparison, it is necessary to calculate the entropy of the substance as a gas, which requires the values for the heat of vaporization, and for the specific heats at higher temperatures. The heat of vaporization may be calculated from the vapor pressure curve. At the present time, recent measurements of these quantities make it possible to calculate the entropy of magnesium vapor.

Experimental Details

The experimental method used is essentially that of the vacuum calorimeter, in which the material whose specific heat is to be measured served as the calorimeter. The apparatus pictured in Fig. 1 was made for a previous investigation[1] and is capable of reaching a temperature of 9.4°A. The bulbs A and B are made of thin glass, bulb B having a *double-walled construction.* The space formed in the double bulb B serves to hold liquid hydrogen, which is condensed by applying several atmospheres' pressure and cooling the outer bulb A with boiling hydrogen. The heat transfer is effected by 2–5-mm. pressure of pure helium in the space between the two bulbs. All other gases are ineffective for this purpose because they are either condensed or are strongly adsorbed at these low temperatures, so that rapid removal by pumping is impossible.[2] When the space between A and B is evacuated by means of a mercury diffusion pump, the inner parts of the apparatus are thermally well insulated. Then if vacuum from a Gaede steel mercury pump and a heavy-duty oil pump in series is applied to the condensed hydrogen so that it boils under 1 mm. pressure, the temperature of the hydrogen decreases rapidly to about 9.4°A.

The block of material to be investigated (K) is suspended freely in a protecting

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[1] Clusius, *Z. physik. Chem.*, Abt. B, 3, 41 (1929).

[2] Eucken, *Sitz. Berl. Akad. Wiss.*, 682 (1914); Clusius and Harteck, Z. *physik. Chem.*, 134,243 (1928).

mantle of copper, which has a block of lead in the upper end to increase its heat capacity. The cable, containing the wires which carry the heating current and the connections to the resistance thermometer, is made of four silk-covered copper wires 0.1 mm. in diameter. The cable, after being wound with thread, was boiled in a mixture of beeswax and resin. No disturbing gases are evolved under vacuum from a cable prepared in this way. To prevent any heat conduction to the block from the outside by the copper wires, the cable is connected thermally with the protecting mantle by imbedding it in a trough of Wood's metal.

In the block of metal a thread-like groove of suitable pitch and depth was cut to accommodate a 0.03 mm. constantan wire having a resistance of 500–800 ohms. Over this winding of the heating element was wrapped a layer of thin tissue paper, which served to insulate the constantan from the next winding of 0.05 mm. lead wire, which formed the resistance thermometer. To give good thermal contact between the block and the two windings, a small amount of lacquer was used. The quantity of lacquer, lead, constantan and paper was determined by weight and considered in the calculation of the specific heat of the metal.

Before undertaking this investigation, the qualifications of the lead resistance thermometer were again carefully determined[3] by comparing its resistance with that of a pure platinum wire between 20 and 80° absolute. The measured resistance of the platinum wire was recalculated by Henning's formula[4] to the exact temperature values given by K. Onnes and Tuyn.[5] The agreement between the lead and platinum thermometers is completely satisfactory considering the difficulty of calibration in this low temperature range.

The completely wound and lacquered block of metal was heated for several hours at 150° in order to harden the lacquer and to age the lead wire, which is necessary for a reproducible resistance value at 0.0°. As can be seen from the following table, a satisfactory behavior of the thermometer was obtained in every case. It was calibrated in the range of liquid air by means of an oxygen vapor-pressure thermometer, and in the range of liquid hydrogen by the boiling point of the latter substance in the chamber of bulb B under a known pressure. The deviations from the normal wire table were limited (maximum 0.1°A.) and were taken into account by means of the Nernst α-rule.[6]

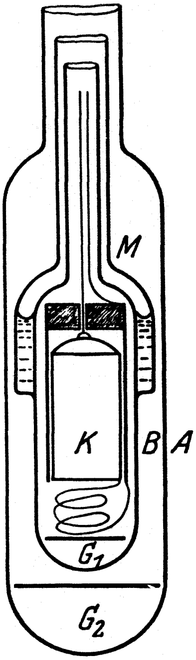

Fig. 1.

Date	Resistance at 0.0°	Sample
1–15–29	277.8 ohms	Magnesium
1–20–29	at 10°A.	
1–28–29	277.7 ohms	
2–5–29	555.0 ohms	Calcium
2–8–29	Used at 10°A.	
2–9–29	555.5 ohms	
2–20–29	134.2 ohms	Thallium I
2–21–29	Used at 10°A.	
2–22–29	134.3 ohms	

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[3] Clusius and Vaughen, *Z. ges. Kalte-Ind.*, 36, 215 (1929).

[4] Henning, *Naturwissenschaften*, 16, 617 (1928).

[5] Onnes and Tuyn, *Comm. Leiden Suppl.*, 58 (1926).

[6] Nernst, Ann. *phys.*, 36, 432 (1911).

Date	Resistance at 0.0°	Sample
4-27-29	200.3 ohms Used at 90°A. 200.3 ohms	Thallium II

The determination of the energy supplied to the sample consisted in measuring the voltage, the resistance of the circuit, and the time of current flow A standardized stop watch was used in an apparatus which made or broke the circuit precisely as the watch was started or stopped. A storage battery of large capacity was used as a source of current. The circuit included a precision resistance box, the potential across the terminals of which was kept constant by balancing it against that of a standard cell. A second standard cell was at times substituted to serve as a check. The e. m. f. of the cell was taken as **1.0185** volts at 20° and a difference between the two cells greater than **0.0002** volt was never detected. The current flow was regulated by means of two parallel sliding resistances, one of which had ten times the resistance of the other. This regulation was not difficult because of the limited change in resistance of the constantan wire due to temperature changes. Before and after each individual heating, the resistance of the constantan wire was determined with an accuracy of 0.1% by means of a precision bridge. The same bridge was used to measure the resistance of the lead wire thermometer. The value, **4.1842** watt seconds = **1** calorie, as given by Jaeger and Steinwehr,[7] was used in the calculation of the heat quantities.

The various sources of error in these measurements are as follows.

(1) Measurement of the Temperature Rise in an Individual Experiment.—The rate at which the temperature increases, due to heat leaks, during the intervals before and after the energy input, was uniform and could be measured accurately even at the lowest temperature. Until after the heat capacity of the sample reached 0.4 calorie, the temperature was read every fifteen seconds. Later readings were taken every thirty seconds.

(2) Error in Determining the Energy Input.—The energy introduced into the sample may be regarded as being correct to within 0.3% for the shorter heating intervals (five to ten seconds), and within 0.03% for the longer intervals (thirty to one hundred twenty seconds).

(3) Error in the Correction for the Accessory Material.—The corrections for the various foreign materials such as the lead wire, constantan wire, thread and lacquer, are as follows.

A = percentage of the total heat capacity due to foreign materials
B = percentage error due to foreign materials

		10°A.	20°A.	80°A.	200°A.
Magnesium	A	39	16	2	2.2
	B	2	0.8	0.1	0.1
Calcium	A	15	5	2	2.5
	B	0.75	0.25	0.1	0.1
Thallium	A	1	.6	1.4	2.2
	B	0.06	.03	0.07	0.1

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[7] Jaeger and Steinwehr, Ber. Sitzungsberichte, **424 (1915).**

(4) Errors in the Measurement of Temperature.—Taking into account the slight error due to the temperature measurement, the total error in the results for calcium at the lowest temperatures probably does not exceed 1.5%. At 20°A. this error amounts to 0.8%, and at 80°A. it is probably within 0.3%. These errors are somewhat lower for the thallium measurements, and are slightly larger for those of magnesium because of the larger error due to corrections for the foreign materials present in the latter sample.

Source of Materials. -The magnesium was presented to us as a very pure sample by Dr. Grützner of the I. G. Farbenindustrie. The analysis of the material is as follows:

Element	Si	Al	Fe	Mn	Cu	Zn	Total
Percentage	0.02	0.06	0.018	0.035	..	..	0.133

The sample of magnesium was turned to a cylindrical block 17 mm. in diameter and 83 mm. long weighing 31.959 g. Considering an atomic weight of 24.32 for magnesium, the block contained 1.316 mole.

The calcium block was of similar dimensions and was turned out of a sample of the purest commercial metal. Traces of iron, silicon, nitrogen and calcium chloride were found by the analysis. The block weighed 28.617 g., corresponding to 0.7139 mole at an atomic weight of 40.07.

Two thallium samples coming from different sources were used in these measurements. No difference in the specific heat curves for these two samples could be detected, which is worthy of mention because our measurements differ from those to be found in the literature. One sample was made by the reduction of pure thallium oxide with charcoal powder in a stream of hydrogen. The other sample came from Kahlbaum, and contained only traces of iron and aluminum according to the analysis furnished. Later, however, the presence of lead was discovered, yet the presence of this element in such limited quantities can hardly have affected the calculation of the specific heat because the atomic weights as well as the characteristic temperature of thallium and lead are similar. In consideration of the appreciably smaller heat conductivity of thallium, blocks of only 12 mm. in diameter and 64 mm. and 47.5 mm., respectively, in length were used. The first sample weighed 84.943 g. (0.4158 mole) and the second 63.671 g. (0.3115 mole), using an atomic weight of 204.39.

Results

The results of these measurements are assembled in Table I, which contains the absolute temperature and the directly measured C_p values. To picture the completeness of the results, the Debye characteristic temperature Θ has been calculated, which required the value of C_v. This value was obtained from the approximate equation[8]

$$C_p - C_v = AC_p^2T$$

In order to use this equation, the value of $C_p - C_v$ must be known exactly for at least one temperature, and since the equation

$$C_p - C_v = T\frac{\alpha^2 V_0^2}{XV}$$

requires data which are not known for calcium and magnesium, the following simplification according to Mie and Grüneisen was used

$$\frac{C_p}{C_v} \simeq 1 + 2.0\ \alpha\ T$$

This equation gives results correct to within 10% for monatomic substances, and the correction here is only about 1.5–2.5% of the C_p value.

The following values were obtained

$$A_{\mathrm{Tl}} = 2.85 \times 10^{-5}$$
$$A_{\mathrm{Ca}} = 2.42 \times 10^{-5}$$
$$A_{\mathrm{Mg}} = 2.61 \times 10^{-5}$$

The 8-values were calculated for values of C_v under 5 calories. Because of the form of the Debye curve, and the increasing errors in C_p and $C_p - C_v$, a further comparison is uncertain.

TABLE I

THALLIUM (TWO SAMPLES)

Sample	$T°$	C_p	C_v	$C_p - C_v$	Θ_D
I	11.18	0.976		...	84
II	11.40	1.069		...	82
I	11.98	1.099		...	85
II	12.64	1.193		...	87
II	12.88	1.234		...	87
I	13.22	1.318		...	87
I	13.94	1.436		...	88
I	13.98	1.552		...	85
II	14.86	1.560		...	90
II	14.93	1.581		...	90
II	15.32	1.637	1.636,	0.001	90
I	15.66	1.743	1.742	.001	90
I	16.08	1.800	1.799	.001	90
II	17.50	1.975	1.973	.002	93
II	17.78	2.009	2 007	.002	94
I	18.24	2.130	2.218	.002	94
II	18.36	2.105	2.103	.002	94

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[8] Cf. "Handbuch der Experimental Physik," Vol. VIII, p. 208.

C_p = Molecular heat at constant pressure
C_v = Molecular heat at constant volume
α = Cubical coefficient of expansion
X = Compressibility
V_0 = Normal volume
V = Volume at the temperature T

Table I (Continued)

Sample	$T°$	C_p	C_v	$C_p - C_v$	Θ_D
I	18.80	2.225	2.222	0.003	93
I	19.86	2.385	2.382	.003	94
II	20.6	2.456	2.453	.003	95
II	20.7	2 457	2.454	.003	96
I	21.7	2.704	2.700	.004	94
II	23.6	3 075	3.069	.006	93
I	25.0	3.176	3.169	.007	95
II	27.5	3.625	3.615	.010	92
I	29.2	3.717	3.706	.011	95
II	33.0	4.105	4.088	.017	94
I	34.5	4.225	4.208	.017	95
II	38.7	4.571	4.548	.023	93
I	40.6	4.675	4.650	.025	93
II	44.9	4.878	4.848	.030	93
I	47.2	4.960	4.927	.033	94
II	52.3	5.175	5.135	.040	92
I	54.0	5.225	5.133	.042	92
II	59.2	5.342	5.294	.048	92
I	61.4	5.319	5.270	.049	97
II	66.1	5.452	5.396	.056	94
I	69.0	5 530	5.470	.060	91
I	77.5	5 632	5.552	.070	93
I	94.0	5.763	5.674	.089	
II	96.2	5.725	5.635	.090	
II	103.5	5 80	5.70	.10	
II	118.4	5 94	5.82	.12	
II	123.2	5.96	5.84	.12	
II	132.8	6.01	5.87	.14	
II	139.8	6 04	5.89	.15	
II	147.8	6 16	6.00	.16	
II	236.6	6.29	6.02	.27	
II	246.6	6.34	6.06	.28	
II	249.0	6 34	6.06	.28	

Magnesium

$T°$	C_p	C_v	$C_p - C_v$	Θ_D
11.31	0.013		...	(450)
11.43	.013		...	(457)
14.14	.026		...	370
14.28	.028		...	364
16.94	.049		...	360
17.24	.051		...	361
19.50	.075		...	360
19.64	.073		...	364
21.7	.112		...	348
24.3	.169		...	340
27.1	.246		...	335
30.2	.353		...	329
34.2	.533		...	323
37.6	.696		...	321

TABLE I (*Continued*)

$T°$	C_p		C	$C_p - C_v$	Θ_D
41.7		0.919		...	319
45.2		1.122		...	319
48.7	1.330		1.328	0.002	318
51.8	1.518		1.515	.003	318
55.1	1.724		1.720	.004	317
63.7	2.214		2.206	.008	318
86.7	3.247		3.223	.024	325
93.2	3.546		3.515	.031	321
99.2	3.718		3.682	.036	324
106.7	3.878		3.836	.042	332
115.4	4.200		4.147	.053	324
124.2	4.426		4.363	.063	321
136.2	4.640		4.564	.076	326
145.4	4.830		4.742	.088	320
163.4	5.070		4 960	.110	319
172.6	5.192		5.071	.121	315
182.0	5.229		5.100	.129	...
191.2	5.329		5.118	.141	...
217.2	5.460		5.291	.169	...
228.4	5.520		5.339	.181	...

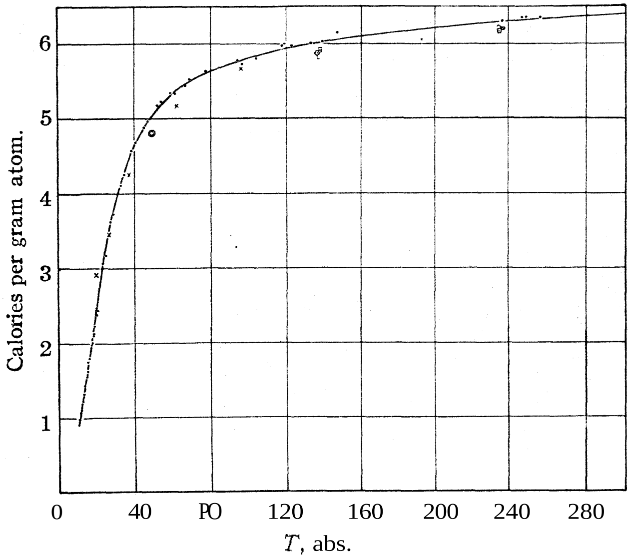
CALCIUM

$T°$	C_p		C_v	$C_p = aT^3$ 4.41×10^{-5}	$C_p - C_v$	Θ_D
10.16		0.044		0.046	...	223
10.66		.055		.053	...	218
11.72		.071		.071	...	220
11.76		.072		.072	...	220
13.02		.097		.097	...	220
13.49		.116		.118	...	215
15.34		.162		.159	...	219
16.58		.203		.201	...	218
17.43		.233		.234	...	219
18.73		.290		.290	...	219
19.36		.320		.320	...	318
21.40		.405		(.432)	...	222
24.2		.581		...	...	221
27.6		.833		...	...	219
31.7		1.094		...	...	226
34.8	1.378		1.376	...	0.002	224
38.8	1.704		1.701	...	.003	225
43.3	2.076		2.072	...	.004	224
52.2	2.744		2.735	...	.009	225
59.6	3.190		3.175	...	.015	227
67.7	3.546		3.525	...	.021	232
75.7	3 879		3.852	...	.027	234
83.5	4.195		4.160	...	.035	233
92.7	4.470		4.425	...	.045	234
102.2	4.700		4.645	...	.055	235
111.5	4.915		4.850	...	.065	233

TABLE I (*Concluded*)

$T°$	C_p	C_v	$C_p = aT^3$ 4.41×10^{-5}	$C_p - C_v$	Θ_D
118.4	5.053	4.980	...	0.073	229
128.6	5.234	5.149	...	.085	...
138.8	5.347	5.251	...	.096	...
147.2	5.480	5.373	...	.107	...
157.0	5.586	5.468	...	.118	...
168.0	5.653	5.523	...	.130	...
178.0	5.779	5.635	...	.144	...
189.4	5.803	5.649	...	.154	...
200.8	5.930	5.763	...	.167	...

Figure 2 presents the curves of the data. The results of earlier investigations are also entered,[9] which in the case of thallium are too low, and with calcium and magnesium are too high, when compared with our data. With samples of thallium from different sources, however, we obtained the same values. The difference between the measurements with calcium and magnesium as recorded here, and those reported by earlier investigators,



Pig. 2.—Thallium: ⊙, Dewar, average; ⊡, Ewald, average; Q , Schimpf, average; X, Nernst and Schwers; ●, Clusius and Vaughen.

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[9] Dewar (Tl, Ca, Mg), *Proc. Roy. Soc.* (London), *89,* 158 (1913); Günther (Ca), *Ann. Pkys.,* [4] *51,* 828 (1916); Eastman and Rodebush (Ca and Mg), THIS JOURNAL, 40,496 (1918); Nordmeyer (Ca), *Verhandl. deut. physik. Ges.,* 10, 202 (1908); Nernst and Schwers (Tl and Mg), *Ber. Sitzb.,* 355 (1914); Richards and Jackson (Tl and Mg), *Z. physik. Chem.,* 70, 414 (1910); Ewald (Tl and Mg), *Ann. Physik,* 44, 1213 (1914); Russell (Tl), *Physik. Z.,* **13,** 59 (1912); Schimpff (Mg), *Z. physik. Chem.,* 71, 257 (1910).

which also differ among themselves, is surely not due to the use of impure samples.

In the case of thallium, direct reproduction of the specific heat values is possible from 17°A. on, by using 0 = 94° in the Debye function. Below this temperature, the 0 value decreases to about 84°, indicating a deceleration of the atomic vibrations. Lead, which is so similar to thallium as regards its elastic constants, its density and its melting point, possesses this characteristic also. With lead, between 20 and 80°A., the specific heat is given correctly by *a* Debye function with a Θ of 88,[10] but at lower temperatures 0 = 85.[11] Keesom and van den Ende,[12] in reporting earlier experiments,[13] mention that at liquid helium temperatures no further variation from the 0-value, determined at 10°A., is apparent.

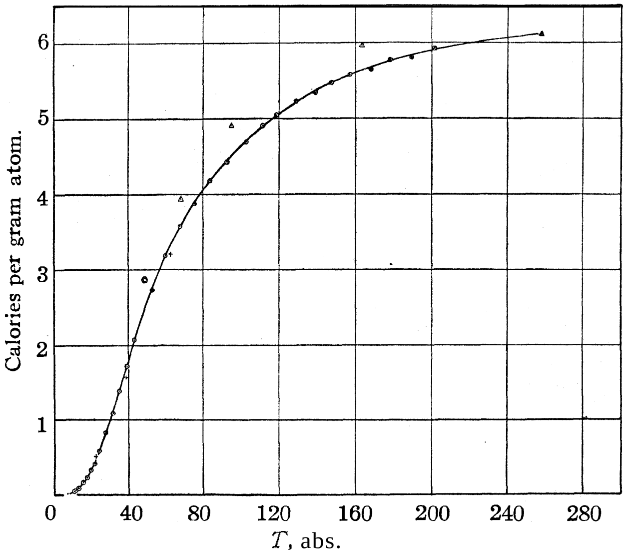

Fig. 3.—Calcium: ◎, Dewar, average; △, **Eastman** and Rodebush; +, **Günther**; ○, Clusius and Vaughen.

In all probability thallium behaves in a similar manner, and an extrapolation of the specific heat curve to the absolute zero (using a Θ value of 84) for the calculation of the absolute entropy, seems justifiable without introducing a large error.

In the measurements with calcium, special care was used in obtaining a high vacuum. Only after several days of continuous pumping did the hydrogen evolution from the calcium block cease. The 0 value of calcium

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[10] Eucken and Schwers, *Verhandl. deut. physik. Ges.*, *15,* **581 (1913).**

[11] Simon, *Z. physik. Chem.*, *110,* **572** *(1924).*

[12] Keesom and van den Ende, *Physik. Z.*, **29,896 (1928).**

[13] Keesom and Andrews, *Comm. Phys. Lab. Univ. Leiden,* No. **185.**

exhibits the comparatively moderate slope of about 6%, **and** therefore belongs to the class of elements whose specific heats are reproduced approximately by the Debye function.[14] Especially noteworthy is the fact that the Θ-value approaches a constant of about 219 at low temperatures, indicating that the T^3 rule of Debye is probably valid. In fact, the data for C_p, calculated from the equation

$$C_p \simeq C_v = 4.41 \times 10^{-5}\, T^3$$

agree remarkably well with the directly measured values of C_p below a C_p value of 0.3 calorie. It appears that the extrapolation to the absolute zero can be performed with safety.

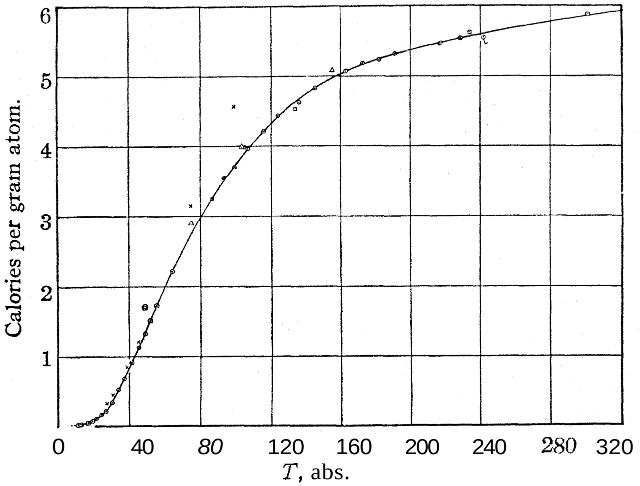

Fig. 4.—Magnesium: ◉, Dewar, average; ⊡, Ewald, average; Q, Schinipf, average; **A,** Eastman and Rodebush; ×, Nernst and Schwers; ⊙, Clusius and Vaughen.

With magnesium, on the other hand, the 0-values increase with decreasing temperature, and above 30°A. a 0-value of 322 reproduces a fairly satisfactory atomic heat value. Even when it is considered that the difficulties of measurement at the low temperatures (due to the extremely small heat capacity of the substance) strongly magnify the possibilities of error, the reality of the effect remains indeed unquestionable. At the lowest temperatures, the points on the curve due to separate series of measurements lie very close together, indicating very good reproducibility. If any appreciable experimental error were present, too high a specific heat value would probably be obtained. A more rapid decrease of the specific heat **curve** than is to be expected from the T^3 law has been noted only in

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[14] Compare the assembly of Professor Eucken in "Handbuch der Experimental Physik," Vol. VIII, p. 245.

the case of copper and tungsten.[15] With copper at 14.51°A., a specific heat of 0.0396 cal. was determined, whereas the calculated value is 0.044 cal. The specific heat of tungsten decreases even more suddenly. The variations with magnesium are of the same order of magnitude. An explanation of this behavior, which might indicate a failure of the fundamental T^3 law, is not at present available.

For the calculation of the entropy under standard conditions, the curves were extrapolated to 298.1°A., by making use of the existing data (see Fig. 2). The following values for the integral $S_0 (S_0 = \int C_p \, \mathrm{d}t/T)$ were obtained.

	Calculated	Lewis and Randall[16]
Thallium S_0	= 15.51	14.6
Calcium S_0	= 9.72	10.64
Magnesium S_0	= 7.76	**8.3**

VAPOR PRESSURE CONSTANTS OF MAGNESIUM

The existing data for magnesium are sufficient to permit the calculation of the vapor pressure constants. The general vapor pressure curve for this element, whose vapor is probably monatomic, is as follows:[17]

$$\log p = -\frac{L_0}{4.573T} + \frac{5}{2}\log T - \frac{1}{4.573}\int_0^T \frac{\mathrm{d}T}{T^2}\int C_{p\text{cond.}}\,\mathrm{d}T + J_p \qquad (1)$$

where p is the saturation pressure at the temperature T, L_0 is the heat of vaporization at the absolute zero, $C_{p\text{cond.}}$ is the specific heat of the condensate, and J_p is the vapor pressure constant. The required values are calculated as follows.

The heat of vaporization at absolute zero may be calculated from the data of Hartmann and Schneider.[18] Since these values were obtained by the boiling method, in which the zone of condensation is located by determining the region of constant temperature, their results may be considered to be free from systematic errors. From the slope of their vapor pressure curve, these authors obtain a value of the heat of vaporization of $L_T = 32{,}800$ calories at an average temperature of 1100°A. Using for the triple point 924°A.,[19] the following is obtained as the heat of vaporization at the absolute zero

$$\bar{L}_T = L_0 + \int_0^T C_{p\text{gas}} \cdot \mathrm{d}T - \int_0^T T\, C_{p\text{cond.}}\,\mathrm{d}T - L_e \qquad (2)$$

$$L_0 = L_T + L_e + \int_0^T C_{p\text{cond.}}\,\mathrm{d}T - 5/2\,RT$$

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[15] Keesom and K. Onnes, Comm *Phys Lab. Univ Leiden,* 147a (Cu); Lange, *Z. physik. Chem.,* 110, 360 (1921) (W).

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

[17] *Cf.* Eucken, "Lehrbuch der Chemischen Physik," 1930, p. 234.

[18] Hartmann and Schneider, *Z. anorg. Chem.,* 180,275 (1929).

[19] Landolt–Bomstein, "Tabellen" Vol. I. 82g (1923).

where L_e is the heat of fusion **(1130 calories)**,[20] C_p is the specific heat of the condensate, which we have supplied for low temperatures, and **for** values above room temperature those reported by Eastman, **Williams** and Young[z1] have been used. The results of these authors are given correctly enough between **300** and 900°A. by the equation $C_p = 2.62 \times 10^{-3} T + 5.27$. The specific heat of the liquid has been taken as 7 **calo**rie~ .Then

$$L_0 = 32800 4 1130 + 7365 - 5965 = 35330 \text{ cal.} \qquad (2a)$$

The logarithm of the triple point vapor pressure is **−0.339** when the value of the saturation pressure at 1163°A. is taken as 84 mm. of mercury according to Hartmann and Schneider

$$\log p_2 - \log p_1 = \frac{L_T}{4.573}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (3)$$

The evaluation of the double integral of Equation 1 is easiest in this case by the transformation

$$\int_0^T \frac{\mathrm{d}T}{T^2}\int_0^T C_p\,\mathrm{d}T = \int_0^T \frac{C_p}{T}\,\mathrm{d}T - \frac{1}{T}\int_0^T C_p\,\mathrm{d}T \qquad (4)$$

The entropy at 298°A. is known as 7.76. The remainder of the equation follows

$$S_{298}^{924} = \int_{298}^{924} 2.62 \times 10^{-3}\,\mathrm{d}T + \int_{298}^{924} \frac{5.27}{T}\,\mathrm{d}T = 7.63$$

The value of the second integral in Equation 4 appears as 5455 calories from the calculation of Lo; therefore the second member of the above equation becomes 5.89. The double integral is then

$$\int_0^T \frac{\mathrm{d}T}{T^2}\int_0^T C_p\,\mathrm{d}T = 7.76 + 7.63 - 5.89 = 9.50$$

Combining the various values in the vapor pressure formula

$$j_p = \frac{35330}{4.573 \times 927} - 2.5 \times 2.967 + \frac{9.50}{4.573} + 0.339$$

$$j_{p\,\mathrm{mm.}} = 3\ 324$$

Calculating the pressure in atmospheres

$$j_{p\,\mathrm{atm}} = 3.324 - \log 760 = 0.443 \pm 0.1$$

The limit of error which has been given is a result of the uncertainty of the energy content of the condensate.

From statistical considerations, the chemical constant value for jk **is**[a3]

$$jk = -1.587 + 1.5 \log M + \log g$$

where M is the atomic weight of the gas, and g is the degree of freedom of the atom in a magnetic field, its quantum weight. For magnesium in particular $g = 1$, and $jk = 0.493$.

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[20] **Auberry and Griffiths, *Proc. Phys. Soc.* (London), 38,378 (1926).**

[21] **Eastman, Williams and Young, THIS JOURNAL, 46, 1178 (1924).**

[22] **Zalesinski and Zulinski, *Bull. intern. l'acad. Polonaise,* 9–10,479 (1928).**

[23] **A. Eucken, "Lehrbuch der chemischen Physik," 1930, pp. 243–248.**

In order to compare the entropy of magnesium vapor, as calculated from these experimental data, with the theoretical value under standard conditions, the data must be rearranged somewhat. Let one mole of magnesium vaporize at 298°A. From Equation 2 the heat of vaporization is

$$L_{298} = 35330 + 298 \times 2.5 \times R - 1155$$
$$= 35655 \text{ calories}$$

if the value 1155 cal. is assigned to the energy content of the condensate (from the specific heat measurements). The entropy increase in vaporizing under equilibrium pressure is $35655/298 = 119.65$ cal. per degree. The equilibrium pressure is obtained from Equations 1 and 4 and from the value of jp.

$$\log p_{298} = \frac{-35330}{4.573 \times 298} + \frac{5}{2}\log 298 - \left(7.76 - \frac{1155}{298}\right)\frac{1}{4.573} + 0.443$$
$$= -25.92_5 + 6.18_6 - 0.84_8 + 0.44_3 = 20.14_4$$

This value corresponds to a vapor pressure of 0.717×10^{-21} atmospheres. In compressing this vapor to atmospheric pressure, the following entropy change takes place

$$AS = -4.573 \times 20.144 = -92.12 \text{ cal. per degree}$$

The entropy of magnesium vapor at 25° is empirically

$$S^{\circ}_{\mathrm{Mg}} = 7.76 + 119.65 - 92.12 = 35.2_9 \text{ cal. per degree}$$

We obtain from the theoretical equation

$$S^{\circ}_{\mathrm{Mg}} \text{ theor.} = 4.573\,ja + 6.699 \times 2.5 \times R = 35.5_2 \text{ cal. per degree}$$

Considering the tendency for double molecule formation, the agreement is satisfactory.

The data necessary for a similar comparison of the spectroscopic and calorimetric values in the cases of calcium and thallium are not at present available. These two metals have transition points somewhere above room temperature that have not been investigated thoroughly. In this Institute, however, experiments are in progress to supply the necessary data.

Many thanks are due Professor Eucken for the use of the property of the Institute, and for his interest and suggestions in the completion of this investigation.

Summary

1. An apparatus is described which was used in measuring specific heats from 10 to 200°A.

2. The specific heats of thallium, calcium and magnesium have been measured from 10 to 200°A. The Debye function has been discussed in the light of these experimental data.

3. The vapor pressure constant of magnesium has been determined as 0.443 ± 0.1 and is found to agree very well with the statistically calculated

value **0.493.** The entropy of monatomic magnesium vapor at atmospheric pressure and 25° has been determined empirically at 35.29 units, while the theoretical value is 35.5_1.

BRESLAU, GERMANY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE INFLUENCE OF THE PERIOD OF HEATING UPON THE BOILING POINT OF CERTAIN LIQUIDS USED IN EBULLIOSCOPY, WITH A NOTE ON TESTING THE PURITY OF VOLATILE LIQUIDS BY ISOTHERMAL DISTILLATION[1]

BY SYDNEY L. WRIGHT, JR., AND ALAN W. C. MENZIES

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This paper describes a series of experiments designed to determine as accurately as possible whether the boiling point of a liquid is dependent upon the liquid's previous thermal history, *i. e.*, whether a liquid which has been boiling for several hours, boils at exactly the same temperature as one recently elevated from a lower temperature. It is obvious, as pointed out by Smits and others, that in associated liquids there might be a delay in attaining the degree of association appropriate to the higher temperature. This would usually result in a slightly higher boiling point at the beginning of ebullition than would be observed several hours later. For purposes of investigation two associated liquids, bromine and acetic acid, and two supposedly non-associated liquids, benzene and carbon tetrachloride, were used.

We also briefly refer to a method of testing the purity of volatile liquids, far more sensitive than the ordinary methods of boiling point and distillation range.

This study was prompted by experiments reported by H. B. Baker,[2] who believed that they demonstrate a delay in the attainment of internal equilibrium in the case of bromine and acetic acid. These observations, if confirmed, might serve to explain several difficulties previously encountered in ebullioscopic work, such as (1) the frequently mentioned necessity of allowing an astonishingly long period of time for the pure solvent to attain a constant boiling point in Beckmann's ebullioscopic method of determining molecular weights,[3] (2) the classical controversy[4]

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[1] From the thesis of Sydney L. Wright, Jr., presented in partial fulfilment of the requirement of the degree of Doctor of Philosophy, 1928.

[2] Baker, *J. Chem. Soc.*, 129, 949 (1927).

[3] Beckmann, *Z. physik. Chem.*, 6, 473 (1890); 8, 225 (1891). Biltz, translated by Jones and King, "Practical Methods for Determining Molecular Weights," 1912, p. 155; Jones, "The Elements of Physical Chemistry," 4th ed., 1915, p. 133; Walker, "Introduction to Physical Chemistry," 9th ed., 1922, p. 200; Findlay, "Practical Physical Chemistry," 4th ed., 1923, p. 264.

[4] Reference to the extensive literature on this subject may be found in Ostwald's "Lehrbuch der Allgemeinen Chemie," Vol. I, p. 308.

as to the equivalence of the static and dynamic methods of vapor pressure determination, (3) the frequency with which it is found that the most satisfactory vapor pressure curve of a liquid shows a temperature at 760 mm. pressure not identical with the best observed boiling point determinations. Raikes and Bowen[5] pertinently remark that this discloses a "situation which can be cleared up only by further research."

Experimental Method

The method in brief consisted of a differential reading between two isoteniscopes,[6] one containing a portion of the liquid which had been held near the boiling point for several hours, the other containing a portion recently rapidly elevated to the same temperature by insertion in the bath. Isoteniscopes, being compact in form, can be used in a bath designed for more adequate stirring than can be supplied for long barometer tubes. This, with the fact that the liquid under consideration is used as a manometric fluid instead of the denser mercury, and that the readings are differential and not absolute in nature, allows a far greater sensitivity[7] than that attained by Baker. The observations were continued until the liquids were more similar in thermal history. A difference in vapor pressure observed at first and not disappearing within a reasonable time must be due not to difference in thermal history but to some of the other factors discussed later.

Apparatus.—The isoteniscopes were constructed of pyrex glass, the bulb of 35-cc. capacity, being sealed to thick-walled tubing of 2 mm. bore which formed the left side of the manometer. The right side was of 10-mm. tubing in which, above the level of the bath, were blown four elongated bulbs to serve as the inner tube of a condenser 27 cm. long. Near the end it was bent at a slightly acute angle to prevent possible contamination from the rubber connections. Each isoteniscope was connected through a short piece of rubber tubing to a tube containing calcium chloride, thence through a long flexible tubing to a 1-liter flask which served as a reservoir to stabilize the pressure and facilitate delicate adjustment. Mercury manometers connected with these flasks were a convenience in manipulation. By means of glass and rubber tubing fitted with suitable clamps, it was possible to establish pressure equality between them, and to adjust both or either of them to any desired pressure not greater than atmospheric The arrangement is shown diagrammatically in Fig. 1.

The bath consisted of a 3-liter beaker filled with glycerin and stirred by a six-bladed glass stirrer electrically propelled. Adjacent were two heating units and the expansion bulb of the thermostat. Near the front of the bath was a bakelite millimeter scale supported vertically. The scale was 120 mm. long and the markings were about 5 cm. wide, so that when the isoteniscopes were in position, the bulbs hung over the top of the scale near the center of the bath, while the manometers, side by side in front of the scale, could be read almost simultaneously. Except for windows at the front and back,

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[5] Raikes and Bowen, "International Critical Tables," Vol. III, 1928, p. 215.

[6] Smith and Menzies, THIS JOURNAL, 32, 1412 (1910).

[7] The sensitivity is illustrated in the last column of Table I, which shows the temperature change corresponding to a pressure change of 1 mm.

the beaker was insulated with cotton wool. A lamp behind the bath furnished illumination. The heating units and the thermostatic control were so connected with rheostats that the difference between the current intensities during the "on" and the "off" periods could be reduced to a minimum at the time of reading, thus diminishing the "pumping" effect referred to later.

Procedure.—Except in the case of bromine (*q. v.*) the liquid was taken up in a dried pipet and 5 cc. placed in each of the thoroughly cleaned and dried isoteniscopes, which were immediately connected to the vacuum system. The permanent gases were removed as far as possible by repeatedly boiling out near room temperature. With water running through the condensers, the isoteniscope was evacuated to a pressure corresponding to the vapor pressure a few degrees above room temperatnre. A small flame was then applied intermittently to the bottom of the bulb. The vapor passed through the manometric portion of the isoteniscope carrying the dissolved gases with it and, condensing, formed a trap which prevented their readmission. By allowing the bulb to cool, the greater part of the liquid was returned to it, leaving sufficient in the manometer to form a trap. When this had been repeated several times with each isoteniscope, comparison in the bath at room temperature showed that their vapor pressures agreed within the experimental error and further boiling out caused no change. After the final comparison, isoteniscope A was removed from the bath and by closing clamp 1 was cut off from the rest of the system. The heat was then turned on and the pressure over the liquid in B allowed to increase as the vapor pressure rose. When the pressure had increased to within a few centimeters of 76, the thermostat was set to hold the bath at the corresponding temperature. The isoteniscopes were allowed to stand thus, A at room temperature, B near the boiling point, for about four hours. The position of the manometric liquid was watched during that time and any necessary adjustments made to prevent the entrance of air into the bulbs. Near the end of this period the pressure on B was reduced slightly so that bubbles of vapor passed through the confining liquid and condensed, thus eventually evaporating all the liquid from the bulb. Meanwhile, by slightly warming A, the liquid in that isoteniscope also was condensed in the wide arm of the manometer. At this point clamp 2 was closed, the connecting tubes evacuated and clamp 1 opened, allowing the pressure on A to be altered without affecting B. Isoteniscope A was then placed in the hot bath and by means of clamp 3 the pressure was increased as rapidly as possible without forcing any liquid into the bulb. When the behavior of the liquid in A indicated that temperature equilibrium was near attainment, clamp 2 was opened, thus assuring the identity of the external pressure on the two isoteniscopes. As rapidly as possible the greater part of the liquid in both isoteniscopes was returned to the bulbs and comparative vapor pressure readings taken. Agitation of the liquid in the bulbs hastened temperature equilibrium. When A was inserted without the precautions noted above, the sudden inflow of heat from the large surface of the

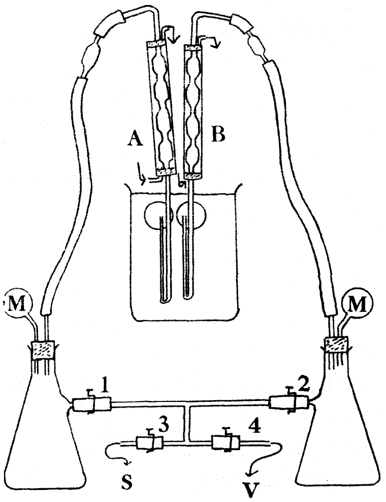

Fig. 1.—Diagram showing apparatus with isoteniscopes in position for reading. A, B, isoteniscopes; 1, 2, 3, 4, clamps; M, mercury manometers used for convenience in adjustment. S, to air; V, to vacuum.

bulb caused instant and complete evaporation, with considerable loss of liquid. This procedure, by reducing the heating surface, allowed the increase of pressure to keep pace with the speed of heating.

The constant "pumping" movement of the manometric liquid due to small fluctuations of bath temperature was reduced as much as possible by proper rheostat adjustment. To minimize the error from this source the reading was made as far as possible at the time of momentary rest between rise and fall of temperature, the pressure being so adjusted that at that instant the menisci in **A** were level. The pressure difference was then read on the manometer of B. When the liquid in the wide arm of B was higher than in the capillary, it indicated that the vapor pressure of **A** was less than that of B. Such readings were recorded as negative. Readings were made at frequent intervals until they became constant, and then occasionally for a longer period.

Isothermal Distillation.—When the readings were completed, it was found advisable to test the purity of the liquids by isothermal distillation. The deficiency of this method as a means of measuring or even detecting impurities has recently been discussed by Washburn.[8] The data forming the basis of his discussion are, however, limited to the difference between the vapor pressure of the liquid with an infinitely large and an infinitely small vapor phase. The method here described, in that it furnishes a few intermediate points, is more promising and was found useful in testing at least the relative purity of the two samples.

The fractionation was generally carried out immediately after the completion of the main experiment, when both samples of liquid were already at the boiling point and supposedly free of permanent gas. By closing clamp 1, and reducing the pressure, bubbles of vapor could be made to pass through the manometer of B and, condensing, increase the volume of the manometric fluid. The speed of this evaporation could be controlled by the amount of change of pressure. By continuous agitation of the liquid in the bulb, and slow rate of evaporation, the condition is approached where the condensing vapor is of the composition in equilibrium with the liquid. At any point the distillation could be interrupted, temperature equilibrium reestablished and the change of vapor pressure in B observed by comparison with A. At the same time, the volume of the liquid in the manometer (previously calibrated against the millimeter scale) was read. Thus, by a series of observations, there could be plotted against the percentage of the original amount of liquid in the bulb, the corresponding reduction in vapor pressure. The points obtained are shown in Fig. 2, in which the lowering is expressed as percentage of saturation vapor pressure which in all cases was close to 760 mm. The points for a sample of acetic acid less pure than that used are included for comparison, as is also a line showing the points to be expected by a liquid containing one mole of a non-volatile solute in 9999 moles of solvent. Where the impurity is volatile, the theoretical curve will vary with each pair of substances according to the behavior of their partial vapor pressures. It may be seen

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[8] Washburn, *Z. physik. Chem.* (Cohen Festband). 592 (1927).

at a glance, however, that the benzene and bromine used in these experiments are of a higher order of purity than the acetic acid.

The most striking feature of this method of isothermal distillation is its sensitivity. Constancy of boiling point, a generally accepted criterion of purity, is crude in comparison, far the acetic acid used, which distilled completely within a range of 0.02°, was found, on isothermal distillation, to show vapor pressure changes up to 58 mm. of acetic acid (used as manometric liquid) in the course of the fractionation.[9] This acid had been subjected to fractional crystallization twelve times, until the melting point became constant within 0.02°, and was then distilled twice, all but a negligible residue coming over within a range of 0.02°, m. p. 16.6°, b. p. 117.8°.[10] These figures are in agreement with the best observations in the literature. In this case, therefore, fractionation as here carried out furnished the only evidence of the impurity undoubtedly present.[11] Im-

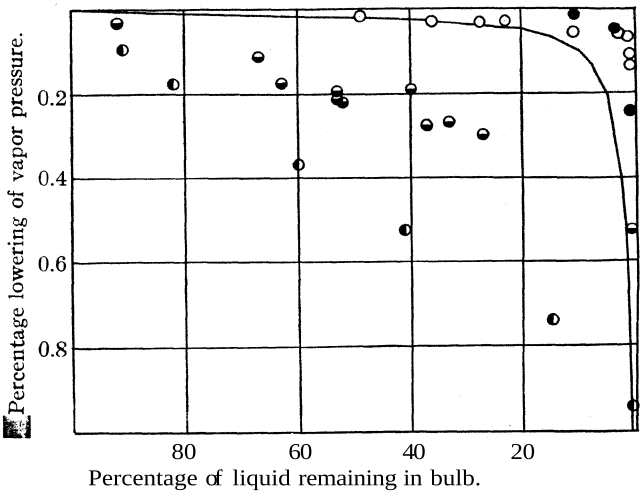

Fig. 2.—Graph showing the fall in vapor pressure resulting in progressive evaporation of liquid by slow isothermal distillation. Fall in vapor pressure is expressed as per cent. of saturation pressure (near 76 cm.). The line represents the theoretical curve for a non-volatile solute. ○, Benzene; ●, bromine; ◒, acetic acid, m. p. 16.6°; ◐, acetic acid, m. p. 16.4°.

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[9] Fifty-eight mm. acetic acid; density 0.94 ≡ 4.0-mm. mercury, density 13.6 ≡ 0.53% of 760 (Fig. 2).

[10] The thermometers used for testing the purity of liquids were compared with a standard thermometer, whose certified accuracy was 0.1°. The constancy of the readings could be estimated more closely as the thermometers were graduated in 0.2". Unless otherwise stated, boiling point observations are corrected to 760 mm. pressure.

[11] Lack of this evidence was undoubtedly the cause of the difficulties encountered by Meyer and Jaeger, *Ber.*, 36, 1555 (1903), and Kahlbaum, *ibid.*, 16, 2479 (1883), in working with acetic acid.

purities, therefore, too small in amount to be detected by ordinary means are capable of causing appreciable error in vapor pressure measurements where the circumstances are favorable to fractionation.

Errors.—Fractionation as a source of error in our results is eliminated by the expedient of evaporating all the liquid from the bulbs of both isoteniscopes immediately before the comparison is made. The liquid on condensing is thoroughly and automatically mixed by bubbles of vapor passing upward through it. On returning the liquid to the bulbs, one is then certain that the vapor pressures observed are those of the whole mixed portions of liquid. Error from parallax was negligible, because it was suffered alike by each limb of the confining liquid within the isoteniscopes; this was tested also by the very close agreement of two isoteniscopes in the bath under like conditions.

The most important single source of error remaining was the constant movement of the manometric liquid in the isoteniscopes. In Table I, Col. 5, is shown the amount of movement that would be caused by a variation of 1° in the bath temperature.

TABLE I

COLLECTED USEFUL DATA

Liquid	Temp. expt., °C.	Density at the b. p., g. per cc.	Factor, mm. liquid to mm. Hg	At normal boiling point p in mm. liquid	
				dp/dt, mm. liq.	dt/dp liq., °C.
Acetic acid	117.5	0.94	0.069	346	0.0029
Bromine	58.8	2.98	.219	115	.0087
Carbon tetrachloride	75.0	1.48	.109	213	.0047
Benzene	78.4	0.81	.060	392	.0026

Actually, by adjustment of the rheostat and making the reading in the manner described, the error of reading the pressure difference at the boiling points was probably not greater than ±1 mm. At room temperature these fluctuations were entirely absent. Temperature variation was significant only on account of this "pumping" effect. The actual temperature of the bath was of importance secondary to that of its constancy of temperature. Traces of impurity, if present in both samples in the same amount, produce no appreciable effect on the differential vapor pressure readings. Minute differences in the amount of impurity in the samples contained in the two isoteniscopes, however, produce considerable effect. Except in the case of bromine there was a possibility of absorption of moisture in transferring the liquids to the isoteniscopes. A greater source of error was the possible presence of permanent gases, even after boiling out and comparing the isoteniscopes at room temperature. Any traces of gas dissolved in the liquid or adsorbed on the inner walls of the isoteniscopes would tend to enter the vapor phase during the heating. Any such accumulation in B would be removed when it was boiled out just before the insertion of A, but in A the heating was of necessity deferred until the readings were to be made and the accumulating gas would cause a gradual increase in the apparent vapor pressure of A as compared to B. This was an error of the second order in all experiments but benzene (a), which was continued for ten hours. In this case a gradual increase of pressure amounting to 0.1 mm. of mercury was noted. Though nearly within the experimental error from other sources, it appeared to be quite definite, and could be accounted for by the liberation of only 0.004 cc. of permanent gas.

TABLE II

EXPERIMENTAL DETAILS FOR ACETIC ACID

Temp., 117.5°; period of heating B, 4 hrs., 50 min.

Time elapsed since insertion of *A* Hrs	Min	Vapor *pressure* diff. *ohs.* Mm liq	Mm HI:	Diff. *in b.* p. *indicated,* °C.
	9	−6	−0.41	+0.017
	12	−4	− .28	+ .012
	8	−2.5	− .17	+ .007
	21	−2.5	− .17	+ .007
	33	−2.5	− 17	+ .007
2	42	−2.0	− .14	+ .006
4	10	−2.5	− .17	+ 007

Results

Detailed experimental data are reported in only one instance for purpose of illustration. The results for all liquids are summarized in Table III. Information not readily tabulated is given under the heading of each liquid. The observations of pressure difference are given to the nearest 0.5 mm., as in some cases, notably those of bromine and carbon tetrachloride, this refinement of measurement has probably some significance, due to a diminished amount of pumping. The time required to heat the bath to the boiling point of the liquid varied from fifteen minutes in the case of bromine to eighty minutes in the case of acetic acid. The period of heating was not considered to have started until the boiling point was attained.

Acetic Acid.—The purity of this material has been discussed. Experimental details are shown in Table II. The pressure difference observed indicated that the more recently heated portion possessed a vapor pressure 0.17 mm. of mercury lower than that heated for about five hours. This is in the direction suggested by Baker's results, but there was no change in this difference over a period of four hours, at which time the thermal history of the two samples was more nearly similar.

Bromine.—This was prepared from recrystallized potassium bromide and purified by the method of Robinson and Briscoe.[12] It was then dried in contact with fused calcium bromide prepared from a portion of the pure bromine. The isoteniscopes were in this case sealed to the drying tube,

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[12] **Robinson and Briscoe, J. *Chem. Soc.*, 127, 142 (1925).**

after which the system was evacuated and allowed to stand for a week. Finally 5 cc. of bromine was distilled into each isoteniscope, which was then sealed off, the tip being later broken after connection to the vacuum system. The desirability of this method of treatment is reflected in the results. The bromine used had not been elevated above room temperature for three months previous to the experiment; vapor pressure 760.5 mm. at 58.8". Isothermal distillation indicated a very high order of purity. There was no difference observed between the pressures of the two samples and no change in this condition over a period of four hours.

Carbon Tetrachloride.—The original liquid boiled at 76.6° within a range of 0.05°. The middle portion was retained and kept for eighteen months in contact with metallic calcium. This was an early experiment, completed before the disturbing effect of fractionation had been observed. In this case, instead of evaporating all the liquid from both bulbs immediately before making the comparison, B was not allowed to boil out, while A of necessity boiled out completely on immersion. No test of purity by isothermal distillation was made.

Benzene.—A high quality commercial product was shaken successively with sulfuric acid, sodium hydroxide and water, and dried over fused calcium chloride. On distillation it boiled at 80.1°. It then stood for twenty-two months at room temperature, for twenty months in contact with metallic calcium and for two months with sodium. Experiment (a) showed a higher vapor pressure in the more recently heated portion, amounting approximately to 0.3 mm. of mercury. The experiment was

TABLE III

SUMMARY OF EXPERIMENTAL WORK

1 Liquid	Acetic acid	Bromine	CCl_4	Benzene	
				(a)	(b)
2 Time liquid in A had remained at room temp., months	2.5	3	18	22	22
3 Time liquid had been held at the boiling point, hours	4.8	4.0	4.5	4.5	19.1
4 Time required for A to attain temp. equilibrium with bath, minutes	12–18	5	6	5	5
5 Duration of expt. after insertion of A, hours	4.2	3.4	0.5	10.0	0.3
6 Av. press. diff. for 15 minutes, mm. liquid first	−2 5	0.0	−1.0	+4.1	+0.8
7 Av. press. diff. for later observations, mm. liquid	−2.3	+0.1	−1.0	+5.8	+0.5
8 Change of press. diff. between 6 and 7, mm. Hg	+0 014	+0.022	0.000	+0.102	−0.018
9 Change in b. p. indicated by 8 in °C	0.0006	0.0009	0.0000	0.0043	0.0008

continued for ten hours, the difference increasing to 0.4 mm. As it was suspected that the original vapor pressure difference was caused by an impurity, both portions of the benzene were subjected to isothermal distillation. The sample contained in isoteniscope B showed good agreement with the other results for benzene, while that in A showed distinctly greater impurity (probably permanent gas). In order to see if this difference disappeared with equally pure samples, experiment (b) was performed. In this experiment the difference in vapor pressure amounted to only 0.06 mm. of mercury, and isothermal distillation showed almost identical curves for the samples in the two isoteniscopes.

Discussion

The following four points (Table III) are most pertinent to the question of whether the phenomenon reported by Baker has any influence on ebullioscopic determinations.

(1) All liquids had been standing at room temperature for a considerable time before being used, thus assuring attainment of the equilibrium for that temperature.

(2) Except in the case of acetic acid, the isoteniscope which had been plunged into the hot bath gained the temperature of the bath in six minutes or less.

(3) The difference in pressure observed varies in direction, suggesting that it is fortuitous. In benzene (a) the difference was accounted for by an impurity found in one of the isoteniscopes. In acetic acid the difference would amount to only 0.007" difference in boiling point. The striking contrast of this result with Baker's is shown in Table IV.

TABLE IV

COMPARISON OF RESULTS WITH ACETIC ACID

Temp. of ohsn., °C.	Pressure difference Mm.	Pressure difference In percentage of satn., press., %	Corresponding temp diff., °C.	Observer
20	2	17	3	Baku
117.5	0.17	0.002	0.007	Wright and Menzies

(4) In all cases but benzene (a) there was no perceptible change in the pressure difference produced by continued comparison over a period of time. The case of benzene (a) has been accounted for by a gradual accumulation of permanent gas.

Summary

To determine whether the boiling point of a liquid is altered by prolonged heating at the boiling point, an apparatus was constructed which allows a direct differential vapor pressure measurement to be made upon two samples of a liquid, one sample having been kept at the boiling point for several hours, the other elevated to the boiling point from room tern-

perature immediately before making the observation. Isothermal distillation within the apparatus furnishes a very sensitive test for the purity of the liquid. As the result of observations made on acetic acid, bromine, benzene and carbon tetrachloride, it may be concluded that the vapor pressure of a sample of liquid rapidly elevated to the boiling point is identical with that which it exerts after remaining for several hours at the boiling point. Delay in attaining internal equilibrium is therefore not a factor of influence in the measurement of boiling point or vapor pressure of these liquids, and observations may be made as soon as temperature equilibrium is established.

PRINCETON, NEW JERSEY

[CONTRIBUTION NO. 38 FROM THE EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY]

THE KINETICS OF THE POLYMERIZATION OF VINYL ACETATE

BY HOWARD W. STARKWEATHER AND GUY B. TAYLOR

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Vinyl acetate forms high polymers on heating alone or in solution, with or without a catalyst.[1] The present investigation indicates that the probable mechanism of the process from monomer to polymer is a type of chain reaction.

The rate of polymerization was observed by measuring the contraction in volume. A linear relation was established between percentage contraction on the original volume of the monomer and the degree of polymerization by density measurements and by evaporating mixtures of monomer and polymers to constant weight, the polymers being nonvolatile.

Apparatus

Dilatometers similar to those used in measuring the thermal expansion of liquids were constructed, consisting of bulbs of 18 mm. tubing and approximately 20 cc. capacity, sealed to straight tubes 4–7 mm. in diameter. The straight tubes were graduated in per cent. Those made from the smaller tubing could be read to 0.02% and the larger one to 0.05%. The thermostats for heating the dilatometers consisted of three large tubes equipped with condensers and filled with boiling benzene, water and toluene. The temperatures of the different baths at the position of the dilatometer bulbs as determined by calibrated thermometers were 82, 101 and 111".

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[1] H. Staudiger, K. Frey and W. Starck, *Ber.*, 60, 1782–92 (1927); Whitby, McNally and Galley, *Trans. Roy. Soc. Can.*, 22, 27–32 (1928). There are also numerous patents on the subject.

Experimental Procedure

The vinyl acetate was distilled, using an ordinary condenser, so that it was exposed to the air. It was kept in a clean tin can to protect it from the light. In some of the measurements the acetate was distilled in vacuum directly into the dilatometer in the all-glass apparatus shown in Fig. 1. The acetate was placed in B and cooled with solid carbon dioxide while the whole apparatus was exhausted with an oil pump. After sealing at E, C was cooled with liquid air or solid carbon dioxide and B allowed to reach room temperature. After collecting a light fraction in C, B was again cooled and D sealed. By a similar procedure another fraction was collected in the dilatometer A, rejecting the heavy fraction left in B. The dilatometer was then sealed off at F.

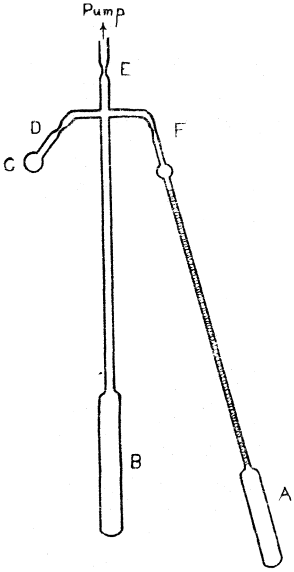

Fig. 1.

In experiments with air-distilled vinyl acetate, alone or in toluene solution, air was pumped out of the diiatometer after cooliig the acetate to −78°. Since the measurements were made at temperatures above the boiling point of the acetate, it was necessary to use a closed system. In preparing toluene solutions definite volumes of vinyl acetate were run from pipets into weighed 100 cc. graduated flasks. They were then filled up to the mark with toluene at 22°. Within the limits of accuracy of this work, no appreciable change in volume was found upon mixing vinyl acetate and toluene.

After a dilatometer had been filled and sealed it was placed in a water-bath at 22° and allowed to stand until the meniscus position was constant. The dilatometer was then placed in the boiling liquid (water, benzene or toluene) bath and the liquid level was read at frequent intervals. In the absence of an added catalyst the level usually rose for the first three to six minutes and then gradually fell. When a catalyst was present the level frequently started to fall by the end of one or two minutes, and the maximum reading was calculated from the reading at 22° and from the expansion as determined in the absence of the catalyst. The dilatometers in most cases were allowed to stay in the bath until no further contraction took place; this required from one to nine days.

Experimental Results

According to Staudinger and others,[1] when vinyl acetate polymerizes it does not yield a single chemical individual but a mixture of polymeric homologous compounds. Our experimental method is justified only if the average density of the mixed polymers is the same throughout the course of the reaction. It is not necessary to treat the reaction product as a chemical individual because we are concerned only with the rate of disappearance of the monomer. Whether the actual densities of all the polymers are nearly the same is not so important in establishing the kinetics of the process as are the differences in density between the monomer and the mixed polymers.

In this study the assumption has been made that all the polymers are non-volatile. In a number of cases, after measuring contractions in the dilatometer, the contents were evaporated to constant weight. Most of the toluene and monomer (b. p. about 60°) were allowed to evaporate at room temperature, and then the sample was kept in a vacuum oven at 65° until it reached constant weight. This required from one to two weeks. The results are given in Table I. Column 4 is calculated from Columns 2 and 3, and Column 6 from Columns 4 and 5. From the table it will be seen that percentage non-volatile (*i. e.*, polymers) is approximately proportional to contraction under widely varying initial concentrations. The experimental error in data of this kind is necessarily high for obvious reasons, but there is no definite trend in the values for percentage polymerization *versus* percentage contraction, so that the average may be accepted.

Table I

Relation between Volatility and Contraction

1	2	3	4	5	6
% by volume of monomer in toluene		Observed % contrac. of soln. at 101°	Calcd. % contrac. in vol. of monomer	% non-volatile on orig. wt. of monomer	% polymerization per % vol. contrac. of vinyl acetate at 101°
At 22°	At 101°				
20	20.55	1.41	6.86	24.5	3.57
		2.83	13.76	46.5	3.38[a]
		3.36	16.35	55.8	3.41[a]
40	40.81	5.28	12.94	45.5	3.52
		9.85	24.14	87.3	3.62[a]
		9.66	23.67	85.2	3.60[a]
60	60.81	12.34	20.29	81.7	4.03
		14.15	23.26	90.1	3.88[a]
		14.39	23.65	91.9	3.89[a]
80	80.56	17.55	21.80	79.6	3.65
100	100	11.16	11.16	43.3	3.88
		19.60	19.60	67.4	3.44
				Average	3.65

[a] Reaction catalyzed with benzoyl peroxide.

From this average, 3.65%, the contraction corresponding to complete polymerization is 27.4%. From density measurements of monomer and polymer at 101°, the calculated contraction is 26.8%, in fair agreement with the above figure of 27.4%. Since determinations of density could be made much more accurately than of non-volatile matter, contractions used in interpreting the data were calculated from them at all three temperatures. Table II gives the measured densities and the contraction calculated from the densities for complete polymerization. As an example of the calculation: 100 g. containing 61.6 g. monomer, at 82°, occupies 100/0.834 = 120 cc., the monomer 61.6/0.85 = 72.5 cc., the polymer 61.6/1.142 = 53.9 cc. The contraction is (72.5 − 53.9)/120 = 15.5%.

Table III summarizes some of the data obtained. The time in minutes

Table II

Contraction Due to Polymerization

% monomer in toluene By vol. at 22°	By wt.	82° Density	82° Contraction, %	101° Density	101° Contraction, %	111° Density	111° Contraction, %
20	21.1			0.798	5.48		
60	61.6	0.834	15.5	.809	16.25	0.798	16.5
80	81.0			.815	21.5		
100	100	.850	25.6	.823	26.8	.812	27.2
Polymers		1.142		1.125		1.116	

is given for each 10% reaction. Results obtained with pure vacuum-distilled vinyl acetate were easily reproducible, but those with the air-distilled material varied appreciably. The reaction with the pure acetate was allowed to proceed at all three temperatures until no more contraction in volume occurred. The densities of the three products thus obtained were determined by weighing in water and air at room temperature and found to be 1.190 ± 0.002. The uniformity in density indicates the same mixture of reaction products at all three temperatures.

Table III

Rates of Polymerization of Vinyl Acetate

% by vol.	Temp., °C.	10	20	30	40	50	60	70	$k \times 10^4$
		Time in minutes to reach indicated % polymerization							
				Vacuum-distilled					
100	82	100	230	375	530	725	1000	1320	11
100	101	20	45	75	112	157	205	261	63
100	111	7.5	16	25	36	49	68	102	140
60	82	200	500	930	1470	2200	..	..	5
60	101	40	88	162	272	400	675	1580	26
60	111	17	40	75	120	200	380	760	62
				Air-distilled					
100	101	5.5	12	19.5	28	40	56.5	88	191
80	101	13	34	65	115	185	320	580	81
60	101	32	105	175	320	600	1340	..	33
20	101	800	3000	[a]	..	..	..	..	..
				1% Benzoyl peroxide					
60	101	..	..	4	..	..	9	16[b]	
20	101	4	8	15	26	49	131	[c]	

[a] 25% in 90 hours. [b] 88% in 16 hours, then no reaction next 3 hours. [c] 61% in 3 hours, then no reaction next 24 hours.

The rate of polymerization of pure vacuum-distilled vinyl acetate approximately follows the law for a unimolecular reaction. Table IV gives the complete data for the run at 101°. The constant, k, was calculated from the formula

$$k = \frac{1}{t} \ln \frac{c}{c - x}$$

where c is the contraction for complete polymerization and x the contraction at time t.

TABLE IV

POLYMERIZATION OF VACUUM-DISTILLED VINYL ACETATE AT 101°

Time, minutes	Dilatometer scale	Contraction, %	$k \times 10^4$
0	126.5[a]		
2	142.2		
3[b]	142.45	0	
8	141.5	.67	50
14	140.4	1.44	50
20	139.3	2.21	51
26	138.2	2.98	51
31	137.4	3.55	51
50	134.6	5.52	49
62	132.9	6.71	49
81	130.5	8.39	48
106	127.7	10.36	47
154	124.1	12.88	43
222	118.5	16.81	45
309	113.2	20.54	48
414	107.4	24.61	61
∞	...	26.8	

[a] At 22° before placing in boiling water jacket. [b] Taken as zero time in computing velocity constant.

Undiluted vinyl acetate gives a fair unimolecular constant in all cases over the entire range. The temperature coefficient for 10° is 2.7 and the heat of activation 25,000 calories, which is the same order of magnitude as for other high-polymer reactions given by Kienle.[2] In toluene solutions the computed values for k fall rapidly with time. For example, take the case of the 80% solution at 101°, the constants figured for each 10% reaction up to 50% are 81, 66, 55, 44, 37 $\times 10^{-4}$. The values of k given in Table III for the toluene solutions are figured for the first 10% reaction, merely as an index of relative speeds at the start.

The effect of benzoyl peroxide upon the rate of polymerization of the 20% solution of vinyl acetate in toluene at 101° is shown in Fig. 2. The rate curves between 190 and 1200 minutes are omitted from the figure. After 1200 minutes, Samples II and III were cooled and more of the peroxide was added. After being replaced in the boiling water-bath, the polymerization rates increased sharply, as shown by the curves. The 1% additional benzoyl peroxide added to Sample II after 1200 minutes gave a curve practically identical in slope with that obtained with Sample V, which contained 1% of the peroxide at the start. In the first 1200 minutes Sample III, containing ten times as much catalyst as Sample II, polymerized only half again as much, and Sample V with 50 times

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[2] R. H. Kienle, *Ind. Eng. Chem.*, 22, 590-594 (1930).

something over twice as much. The curves show, in general, that a given amount of catalyst causes the same degree of polymerization, whether added all at once or in portions at successive time intervals.

In no case did the reaction in toluene solutions go to completion although in some experiments the heating was continued for nine days. It is perhaps significant that in the uncatalyzed reactions the polymerization of 40, 60 and 80% solutions apparently stopped when they contained approximately 2.0 moles of monomer per liter, while the polymerization of the 20% solution appeared to stop when it contained 1.5 moles of monomer per liter.

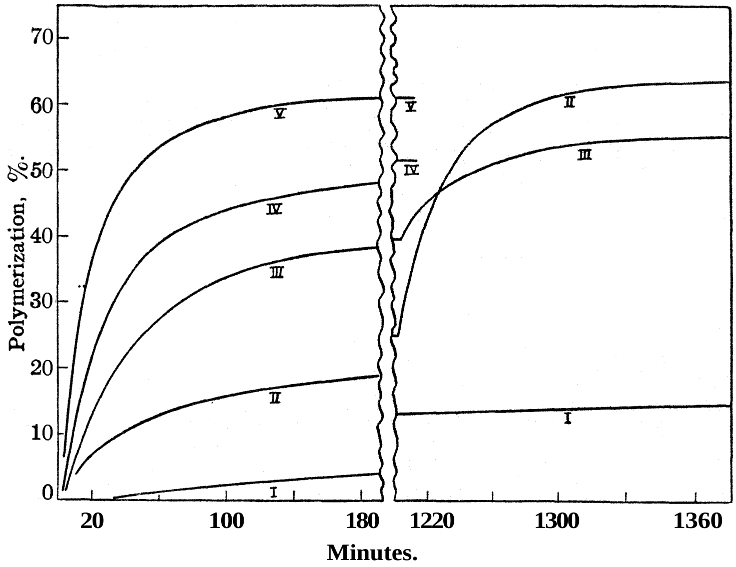

Fig. 2.—Polymerization of 20% vinyl acetate in toluene (101°). Percentage of benzoyl peroxide: I. 0.00; II, 0.02 and 1.0; III, 0.2 and 0.2; IV, 0.4; V, 1.0.

There are negative as well as positive catalysts for this polymerization. A sample of air-distilled vinyl acetate containing 1% of sulfur was heated for twenty hours in boiling water with no detectable contraction in volume. If no sulfur had been added, polymerization would have been essentially complete. This effect of sulfur had been determined previously by Blaikie.[3]

Discussion of Results

It seems likely that we are dealing with a chain reaction of some kind. The reaction involves the combination of many molecules to form a polymer and yet it follows the unimolecular reaction rate law. The explana-

[3] Blaikie, Canadian Patent 282,860 (1928).

tion is probably similar to that put forward by Christiansen and Kramers[4] to explain a simpler type of pseudo-unimolecular reaction. In this theory an activated molecule is formed for every one that reacts.

Benzoyl peroxide acts as a trigger catalyst in starting reaction chains and is itself destroyed in the process, since chemical tests always showed its absence when the catalyzed reaction stopped. Anti-catalysts, like sulfur, interrupt the reaction chains. The inhibition of the reaction by toluene may be explained on the basis that activated molecules give up their energy to the toluene molecules before they can combine with other vinyl acetate molecules. In other words, the toluene has the same effect in breaking reaction chains that walls exhibit in some homogeneous gas reactions.

Summary

The polymerization of pure vinyl acetate is shown to follow the unimolecular rate law. In toluene solution the rate of reaction is retarded. The kinetics of the polymerization are explained on the basis of a chain reaction. Benzoyl peroxide acts as a trigger catalyst by initiating reaction chains. Sulfur inhibits the reaction.

WILMINGTON, DELAWARE

[COMMUNICATION NO. 439 FROM THE KODAK RESEARCH LABORATORIES]

THE VACUUM FRACTIONATION OF PHLEGMATIC LIQUIDS

BY K. HICKMAN AND W. WEYERTS

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In the course of some work on heavy oils the need has been encountered for an adjective which will convey the sense of "difficultly volatile" or "high boiling." Instead of inventing a word we have prepared to adapt a word which is already well known and, therefore, nearly self-explanatory. Such a word is "phlegmatic." Derived from the Greek φλεγματικός, the original suggestion of "fieryness" has given place to the well-accepted sense of sluggishness, apathy or resistance to disturbance. Phlegmatic seems a particularly suitable word to denote high-boiling properties, and it is the adjective which will be used throughout this paper.

Many separations of phlegmatic liquids by fractional distillation could be performed more efficiently or more conveniently[1] at very low pressures if it were not for the uncertainty concerning the real pressure in the distilling

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[4] Christiansen and Kramers, *Z. physik.* Chem., **104, 451 (1923).** See also Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Clarendon Press, Oxford, 1929, Chapters V and VI.

[1] Bumping vanishes entirely at pressures below 1 mm.

apparatus. Where simple distillation is concerned, without reference to the temperature at which it occurs, high vacuum can be employed.[2] Where the temperature–pressure relation is important, as it is in fractionation, or in determining the purity of a distillate, or in identifying a material by its boiling point, then relatively poor vacua have hitherto been compulsory. It is safe to say that any boiling point recorded in the literature from ordinary distillations at 10 mm. is probably inaccurate by 1°, and boiling points expressed at lower pressures are completely unreliable.

This unreliability is due chiefly to the lack of uniformity of pressures in the distillation apparatus. In using gaseous systems at atmospheric pressure it is usually assumed that the pressures are identical at all parts of the apparatus; a gage attached at any part will give information relating to the whole. Where the internal conditions are dynamic rather than static, owing to a flow of gases from one portion to another, the pressures no longer are equal in all parts, a difference of a millimeter or so arising in the effort necessary to move the gases. The difference may be less than one-tenth of one per cent. of the total pressure, and is usually neglected. Under high vacuum conditions a difference of one millimeter may cause a difference of a thousand magnitudes in the density of gases in various parts of the system. Measurements of vapor tension taken at an appreciable distance from the thermometer region may be entirely untrustworthy.

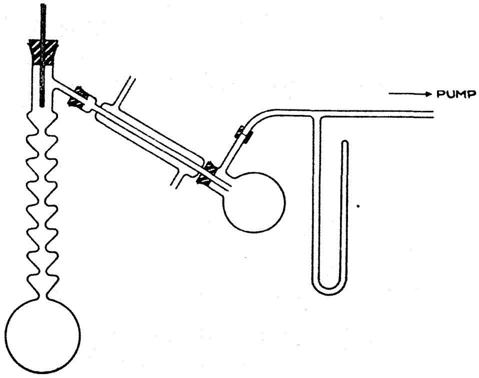

Fig. 1.

A full discussion of the factors contributing to false pressure readings has been given in a previous paper.[2] It will be more useful now to recall the phenomena which usually occur during the low pressure distillation of an organic liquid in the conventional distilling flask and condensing arrangements. In Fig. 1 a flask with rectifying column is shown connected by a side tube with a water-cooled condenser, *a* receiver, a manometer and an exhaust pump; a thermometer projects into the rectifying column to just below the exit tube.

We will place in the flask some comparatively phlegmatic liquid and commence distilling at a reduced pressure. **A** good material to distil would be butyl benzoate. With the pressure at 60 mm., vapor would pass over excellently at 170°. At 20 mm. the thermometer would register 132'; at 10 mm. 117°; at 5 mm. 104'; at 3 mm. 97°; at 1 mm. 92° and at

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[2] Hickman *and Sanford, J. Phys. Chem.*, **34, 637 (1930).**

0.0 mm. 90°. Now it is apparent that if the temperature–pressure relation which subsists from 60 to 10 mm. still holds, as we have every confidence that it does, the temperature at 0.0 mm. pressure should be about absolute zero. The usual mercury manometer cannot be read with the naked eye below 0.1 mm., but even at this pressure the boiling point of butyl benzoate should be less than 50°. Furthermore, the discrepancy in boiling point is not constant. If, with the manometer still reading substantially zero, the heat is increased under the distilling flask, the mercury in the thermometer may rise 5 or 10°; if the heat input is decreased, it will fall.

The temperature measurements, within limits, are beyond reproach, but the pressure measurements are faulty. If the thermometer registers 60°, the pressure of a saturated vapor of butyl benzoate around the thermometer bulb must be about 1 mm. This vapor then passes into the condenser and turns into liquid in equilibrium with a vapor at such negligibly small pressure that for our present purposes it is zero. More vapor from the flask continues to flow into this empty space, and the temperature at the thermometer of 60" is a measure of the pressure (1 mm.) which is necessary to force the quantity of vapor which survives each moment, into the passage from the flask, through the side tube and into the condenser. Supply more heat at the flask, and the pressure must rise to drive over the larger quantity of vapor.

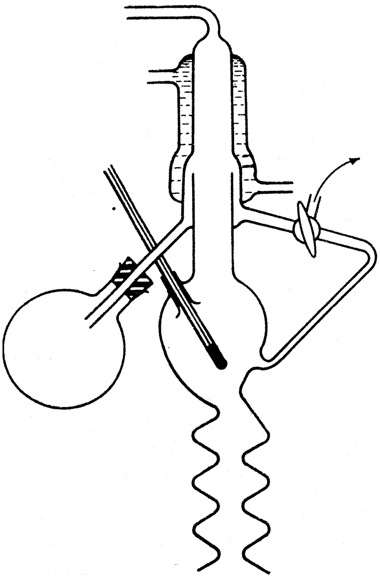

Fig. 2.

Many partial remedies will occur to the reader but drastic alterations to the equipment are required for a complete cure.

Two conditions should be satisfied if the data are to be recorded correctly. The thermometer should be placed in an expansion of the column where the vapor has a relatively small velocity, and the manometer should operate directly from the wall of this expansion. No passage filled with gas can communicate the pressure with an outside gageunless this passage and the pressure recording mechanism at the end of it are kept at the same temperature as the bulb.

It is simpler, therefore, to use a small portion of the condensate as it flows down the walls of the bulb as a manometric fluid and to provide a glass tube and recording scale at a convenient point on the bulb. The pressure side, however, is only one-half of a manometer, and it is necessary to produce a substantially perfect vacuum at the other end.[3] This would mean, since the filling is to be of the material distilled, that the high vacuum must be applied whenever wanted, presumably by a separate pump. The complication can be avoided by forming the condenser into a simple condensation pump, so that the vapor under treatment produces its own reference vacuum. We have given a still head (Fig. 2) modeled in this manner prolonged trial in the laboratory and have found that with liquids of the class for which it was intended the head never failed to yield a better reference vacuum than could be communicated through the three-way stopcock from a separate pump.

The differing capillary actions at the ends of the self-contained manometer require that the zero point be found empirically by momentarily relieving the vacuum so that the liquid may equalize in the two limbs. The liquid in the automanometer requires scavenging frequently if the condensate varies in volatility or density as distillation proceeds.

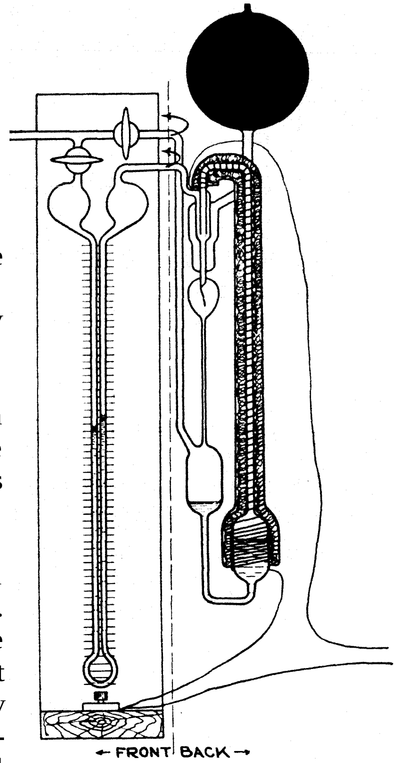

Fig. 3.

The still head can act as a diffusion pump only if the pressure at the exit tube to the exhaust pump is considerably less than the pressure of vapor in the thermometer cavity and thus at the male jet. It is therefore quite essential to have a sensitive manometer in the exhaust line. A McLeod gage and possibly a Pirani gage could be used, but we favor a direct reading liquid manometer. The mercury manometer is unreliable because of difficulty of reading minute changes in level and because of the doubt which must always exist as to the perfection of the reference vacuum in the closed limb. We have devised a butyl phthalate filled manometer which, although of somewhat complicated design, is simple and entirely reliable in use. It is illustrated in Fig. 3 and is described in an appendix to this paper.

[3] If the temperature of the liquid in the vacuum end is 80° less than at the pressure end, the vapor pressure will generally have decreased a thousand times and may be neglected. In chemical vacuum work it is a useful rule that any liquid which is under distillation may itself be used cold as a manometric fluid, as a joint seal and as a film to prevent the escape of volatile matter from the inside of rubber pressure tube and from corks. We repeatedly perform distillations in special apparatus at 0.1 micron using matured rubber stoppers and rubber tubes soaked in the phlegmatic liquid under treatment.

The condensation still of Fig. 2 will only accommodate vapor pressures up to 1 mm. and liquids to be condensed at 10 and 20 mm. will not generally survive on the high vacuum side of the jet unless the condenser is maintained many degrees below zero centigrade. It then becomes convenient to operate with a positive air pressure in the system and attach an external phthalate manometer to the free arm at the three-way stopcock of Fig. 2. The pressure difference between the thermometer cavity and the condenser is then added to the pressure registered by the external manometer and the sum is the pressure at which the liquid is condensing.

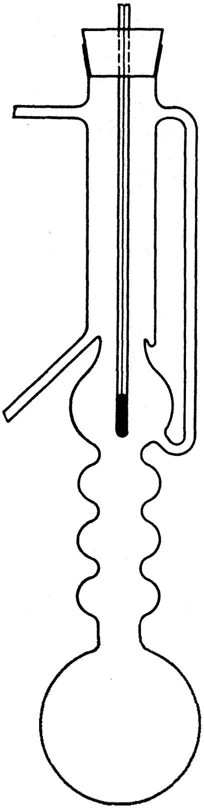
Fig. 4.

A very convenient unit for the accurate distillation of small samples ranging from 5 to 100 g. is that shown in Fig. 4. The thermometer bulb hangs in the largest cavity of the dephlegmating column and a side manometer tube passes from the lower region of the cavity to the top of the condensing chamber. The latter may be water cooled, but it is generally sufficient to employ the draught from a small fan. The condensate collects in the annulus and flows out of the delivery tube to the left. The correct boiling point at regions of rapid change of boiling point can be secured by preventing the distillate from escaping. It then collects in the annulus and flows back down the column. When the boiling point has been secured the side tube is unclipped and collection of the distillate resumed. Care must be taken that the cool distillate does not run down the thermometer bulb from the annulus. The pressure in the thermometer cavity is, of course, the sum of the pressure in an external manometer and in the automanometer.

The measurement of pressure by an external manometer becomes more and more accurate as the cavity housing the thermometer and the passage therefrom to the condenser become larger. We thought, at one time, that the automanometer construction could be abandoned in lieu of another suitable design. It was soon found that very large openings allowed the vapor–air junction to oscillate in position, at one moment leaving the thermometer uncovered, at another heating the stem many centimeters up. The apparent boiling point would fluctuate correspondingly. It was preferable to confine the vapors in the cavity and allow them to issue into the vacuum system under a small positive pressure. The vacuum system **then** became a comparatively inexhaustible reservoir waiting to receive products of decomposition or traces of volatile solvents. **A** much smaller vacuum bottle could be used in series with the **pump** to steady the pressure.

It may be inquired which of the columns described is the most useful. Our first choice would be the device pictured in Fig. 3. It may be noted that the point of novelty on which this paper is based is the application of a side tube near the thermometer region of any distilling flask. If the glass blowing difficulties are found insurmountable, quite good work can be done with the simple set-up pictured in Fig. 5.

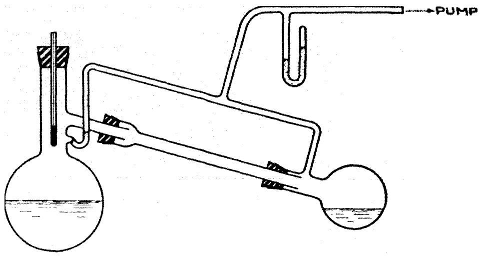

Fig. 5.

Experimental

Distillations were performed in flasks of the type shown in Fig. 1. Two flasks were used, one with a side arm of usual bore, and one with a side arm of as large diameter as the neck of the flask itself. Butyl benzoate was employed as the liquid, and was boiled by an electric heater at three different wattage inputs. The boiling points at each apparent pressure, as registered by an external manometer, are recorded in Table I. The real boiling points corresponding to the recorded pressure are included for comparison and all the data are summarized in Figs. 6 to 8. It will be noticed

TABLE I

DISTILLATION DATA

Boiling points in °C.

Type of still	Watts input	Pressure, mm., in condenser, read by phthalate manometer 20	10	5	3	2	1	0.03	Distillation rate, drops per min.
Fig. 1, small side arm	40	131 6	116.8	104.4	98.8	95.8	95.8	95.2	30, start; 47, finish
	50	132 0	117.3	106.2	102.8	102.4	101 5	100.0	60–80
	60	132.3	117.8	107.9	106.5	106.5	...	...	69-95
Fig. 1, large side arm	40	131.6	116.7	102.9	97.4	92.2	85.8	84.8	...
	50[a]	132.0	117.4	104.0	99.2	92.9	90.5	90.4	...
	60	132.8	117.0	103.1	99.4	94.0	88.7	88 1	...
Fig. 3, condensation still	Variable	131.5	116.0	102.5	93 0	86.5	75.5	67.8	70
	to keep	At	At	At	At	At	At	At	
	distn. rate	135	110	99	95	87	70	60	...
	const.	watts	watts	watts	watts	watts	watts	watts	
True pressures in condensation still, thermometer cavity	....	20 mm.	10.01	5.02	3.05	2.07	1.14	0.65	...
True boiling points at the pressures in the top of horizontal column	....	131.5	116.0	102.5	92.8	86.0	74 3	24.7	...

[a] An interval of ten to fifteen minutes was allowed after each adjustment of heat input to allow a steady distillation rate to be reached. In the case marked with the a readings were taken after a few minutes only. Their divergence from the other series shows how sensitive to external conditions are these low-pressure distillations.

that the true boiling point of **131.5** at **20** mm. was disturbed by less than a degree at reasonable rates of distillation. A maximum discrepancy of a degree and a half occurred at 10 mm. pressure but the errors became serious at **5** mm. The large side arm flask gave an average inaccuracy of 5° at **3** mm., and the readings were valueless below this pressure. The narrow arm flask failed substantially at 5 mm.

As a second exercise, a sample of commercial a-chloronaphthalene was distilled in the still of Fig. **3.** The sum of the pressures in the external manometer and the automanometer was kept at **10** mm. This ensured a pressure of exactly 10 mm. in the thermometer cavity.

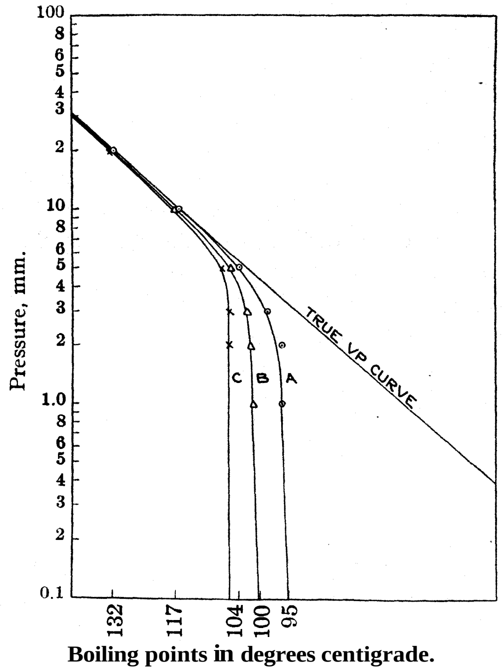

Fig. 6.—*n*-Butyl benzoate, Type of still, Fig. 1, small side arm. A, 40 watts; B, 50 watts; C, 60 watts.

The variation of temperature with the progress of distillation is shown in Fig. 9. It will be noticed that the points fall very smoothly on the curve drawn through them, indicating that little difficulty was encountered in obtaining true readings. The steep rise at the end of distillation is significant. The rise had to be accompanied with a corresponding increase of heat input to keep the pressure constant in the automanometer. Had the distillation been performed in an ordinary flask the real great rise in boiling point of the later fractions would have yielded a small apparent rise and the rate of distillation would have diminished until the pressure in the thermometer region had fallen sufficiently to convey the more phlegmatic vapor over with the same heat content. No indication of this would have been visible at the external manometer.

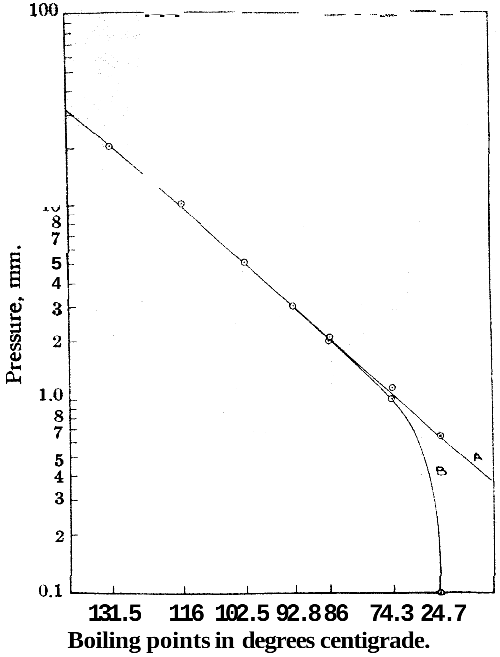

Fig. 7.—*n*-Butyl benzoate. Type of still, Fig. 2, condensation pump. Curve A, pressure read from external manometer plus pressure in automanometer, giving true pressure–temperature relation. Curve B, external manometer readings, yielding false pressure–temperature relation.

TABLE II

EXPERIMENTAL DATA

True pressure = sum of external manometer readings + automanometer readings	External manometer readings	Automanometer readings, corrected to mm.	Temperature, °C.
10	6.65	3.35	118.9
9	5.65	3.35	116.1
8	4.65	3.35	113.4
7	3.65	3.35	110.3
6	2.65	3.35	107.2
5	1.65	3.35	103.2
4	0.65	3.95	98.7
3	.05	2.95	93.8
2	.05	1.95	85.8
1	.05	0.95	71.3

The composition of the distillate was fairly constant from 20 cc. to 40 cc., and as a further exercise the material was returned to the flask and distillation recommenced until 30 cc. had passed over. A by-pass tube was then inserted so that distillation could proceed cyclically, the material condensing being allowed to flow back into the still. The variation of boiling point with alteration of pressure was then examined and the data recorded in Table II. Figure 10 shows the correct and incorrect pressure–temperature curves drawn from these data. The bent, incorrect curve is the one which would ordinarily have been obtained if the automanometer device had not been employed to correct the pressures read by the external manometer.

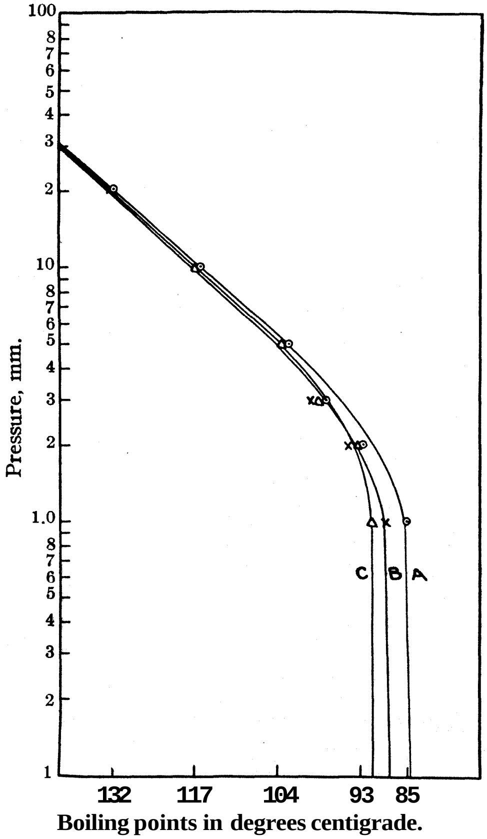

Fig. 8.—n-Butyl benzoate. Type of still, Fig. 1, large side arm. Curve A, 40 watts; B, 50 watts; C, 60 watts.

It would be impressive to perform a separation of two liquids under vacuum in an ordinary distilling flask and then show the improved result by using our special apparatus, but after the ample proof of discrepancy which we have already given such a course seems hardly worth while. Instead, a separation of two liquids, butyl benzoate and ethyl phthalate mixed in equal proportions, has been made in a flask with a *wide* side tube (Fig. 1, and Table I, subdivision 2), and this separation has been compared with that obtained with the condensation still of Fig. 2. The wide side tube still was operated with 0.1 mm. pressure in the condenser first at constant voltage input (Curve A, Fig. 11), and then at an attempted constant distillation rate (Curve B), but no steady thermometer readings could be obtained. An absolutely constant distillation rate was difficult to secure, and the slightest variation altered the thermometer readings by many degrees. The false maximum at 80 cc. is due to this cause. At 10 mm. (Curve C) better results were obtained. The excellent separations secured at 0.65 mm. and at 10 mm. in the condensation still are shown in Fig. 12. The temperatures are as concordant at a fraction of a millimeter as at 10 mm. The operator would have no difficulty in deciding where to make cuts or what the exact temperature–pressure relation was at each cut.

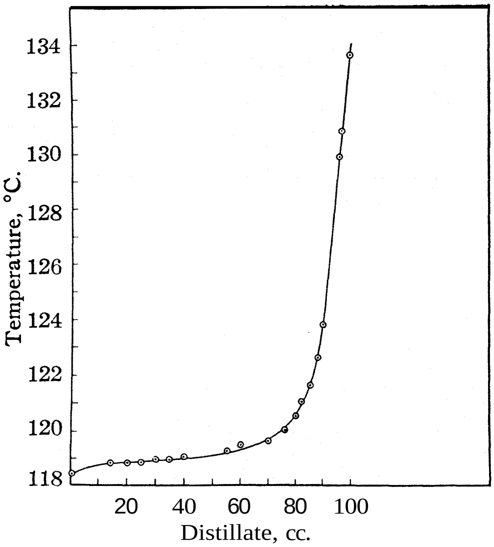

Fig. 9.—α-Chloronaphthalene, 10 mm. of mercury.

As a final exercise, about fifteen organic liquids were distilled which had boiling points ranging from 60 to 200° at less than 20 mm. pressure. The samples showed boiling points which were, in general, considerably lower than those stated in the literature.

Further Considerations.—The fall of pressure existing at the jet is not the only pressure difference within the still during distillation. At each constriction in the dephlegmating column there is a readily measurable drop in pressure which may give useful information. The early experimental column of the type shown in Fig. 2 had six manometers and corresponding thermometers inserted, but was later abandoned in favor of a distillation unit with only three thermometers: One in the liquid in the boiling flask, one in the lowest bulb of the column, and the third in the top bulb before the condensation head. Differences in reading between the bottom and middle thermometer indicated the purity of the liquid, while the top and middle thermometers coupled with manometer readings gave, when plotted with pressures against inverse of temperature, a good indication of the slope of the vapor-pressure curve for each fraction.

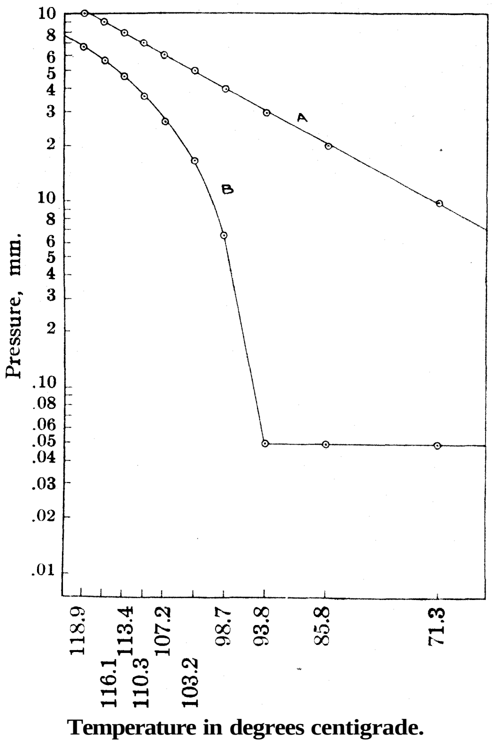

Fig. 10.—A, true temperature–pressure relation obtained by plotting the true pressures (sum of external manometer readings and automanometer readings) against the reciprocals of the absolute temperature. B, false temperature–pressure relation obtained by plotting the apparent pressures (external manometer readings) against the reciprocals of the absolute temperatures.

In the general reaction Aa + Bb = AB + ab where AB is a much larger molecule than ab, it is unlikely that either Aa, Bb or ab, will have the same slope of vapor pressure curve as AB, which will often be steeper, showing a greater depression of vapor pressure as the temperature falls. It is therefore an advantage to have a sheet of graph paper at hand while distilling, and plot the two or three pressure–temperature points for each fraction. The divergence in slope of the connecting lines will show whether a better separation is likely to occur when the pressure is raised or when it is lowered. Often the separation is better at the lowest pressures.

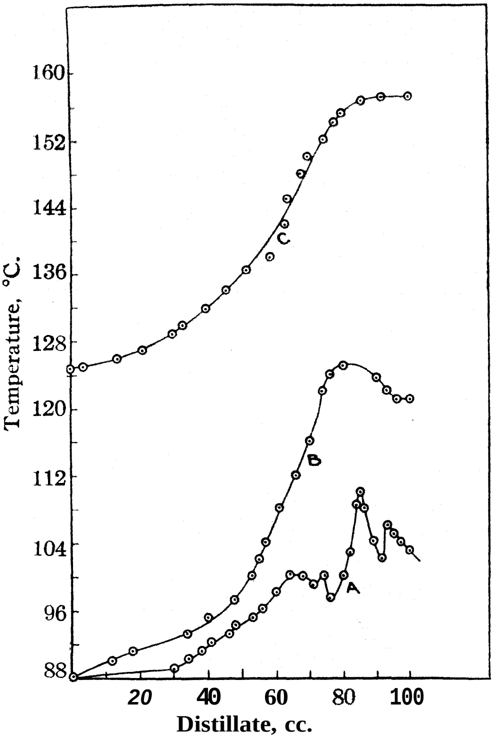

Fig. 11.—Mixture of *N* butyl benzoate + ethyl phthalate, type of still, Fig. 1, large side arm. A, at 0.1 mm. Hg heat input was held constant throughout; B, at 0.1 mm. Hg heat input variable, distillation rate constant; C, at 10 mm. Hg heat input was held constant throughout.

The purification of commercial butyl phthalate is a case in point. The likely impurities are butyl alcohol, butyric acid, phthalic anhydride and butylphthalic acid. At pressures above 20 mm a constant-boiling mixture distils, which, although it contains over 90% of butyl phthalate. is useless for vacuum pump purposes. When the distillation is performed at

0.64 mm. the butyl alcohol and butyric acid are sucked into the pump, the phthalic anhydride, which now boils at a lower temperature than the phthalate, deposits in a crystalline mass in the condenser, from which position it may be washed down with the first runnings of phthalate. A large middle fraction of pure butyl phthalate comes over, leaving a residue of butyl phthalate and butylphthalic acid which could be worked up under a lower pressure were it not that the crude phthalate is less expensive than the labor involved.

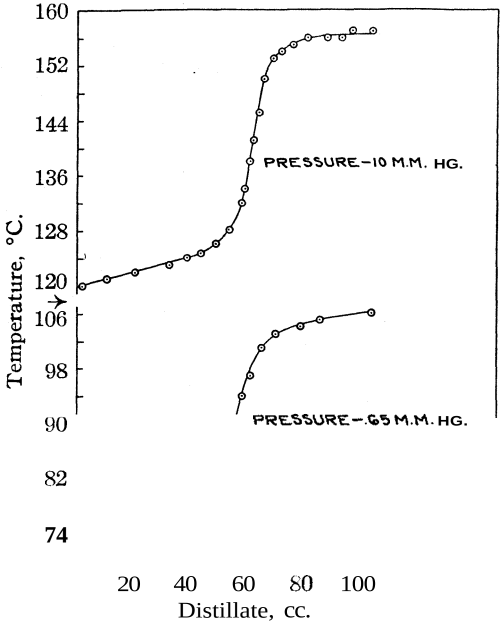

Fig. 12.—Mixture of n-butyl benzoate and ethyl phthalate, type of still, Fig. 3.

The statement that the phthalate was distilled at 0.64 mm. is derived from a knowledge that the specific gravity of *n*-dibutyl phthalate is 1.014 at 25° and that the column in the manometer attached to the thermometer cavity was 8.5 mm. high, whence

$$\frac{1.014 \times 8.5}{13.5} = 0.64 \text{ mm.}$$

A convenient way to describe the boiling point of any pure liquid would be in terms of the vapor pressure needed to support a unit height of a column of its own substance. Thus, butyl phthalate boils at 138° at a pressure supporting a column 8.5 mm. high of liquid butyl phthalate. We can denote this pressure by some convenient term, such as auto-pressure, and use the abbreviation A. P. Butyl phthalate boils at 138° at 0.64

mm., or 138° at 8.5 mm. **A. P.** Such a system of nomenclature would allow the pressure of any homogeneously boiling liquid to be described in conveniently-sized length units which are repeatable by anyone else without reference to tables. For conversion to the common mercury pressure scale, it is necessary to know the specific gravity of the liquid. Part of any pure preparation may be reserved for such a determination. A convenient means for securing approximate information of sufficient accuracy for the work is shown in Fig. **13.** Distilled water and the liquid are placed, one in each cup, and slight suction applied by the rubber ball. The liquid rises to a characteristic height which may be compared with the height of the water column. The menisci at the lower ends of the U-tubes compensate for surface tension errors.

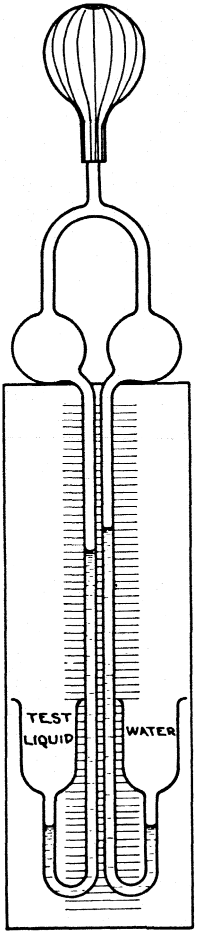

Fig. 13.

We have encountered an interesting source of error. As the liquids become very pure the surface tension alters and the liquid may cease to wet glass. Certain samples of benzyl phthalate appeared to suffer a sudden diminution of vapor tension. The liquid receded in the manometer and the meniscus flattened, occasionally becoming convex like mercury. Touching the tube with a lighted match caused the liquid to flow evenly and resume its normal position. It is necessary to be sure that the liquid under treatment thoroughly wets the manometer. It may be useful to recapitulate the factors which contribute to securing correct boiling points. They are: **(1)** a dephlegmating column between flask and thermometer to remove superheated vapors; (2) a cavity or expansion in the column where the thermometer bulb is situated; **(3)** a limited opening between the thermometer cavity and the condenser; (4) a manometer situated on the side of the thermometer cavity and operated by the condensate; (5) a sensitive external manometer.

Summary

It has been shown that the usual distillation apparatus does not give true boiling points at low pressures.

Apparatus has been described which enables true boiling points to be secured.

A number of distillation experiments under vacuum have been described. A system of nomenclature for high boiling liquids has been suggested.

APPENDIX

A DIRECT READING OIL MANOMETER

Referring to Fig. **3,** a simple U-tube is protected with splash bulbs at either end and is connected on the left-hand measuring side through a well-ground stopcock to the vacuum line. The other limb, in which a comparatively perfect reference vacuum is to be maintained, is connected with a miniature butyl phthalate condensation pump. The jets of this pump are only three or four millimeters in diameter and are surrounded by a cooling jacket communicating with a relatively large bulb painted black and situated above the main structure. The jacket is just completely filled with alcohol, the bulb is evacuated of all but the saturated vapor above the liquid and is then sealed off in the blow pipe flame. Hot vapors condensing at the jet cause the alcohol to boil at slightly above room temperature and send vapors into the flask, where they condense and return as liquid. The large surface of the bulb then becomes available for radiating the heat passing through the small surface of the pump. The jets are supplied with phthalate vapor through an electrically warmed and lagged tube from a boiling bulb some distance below. The condensate with entrained gases falls down a narrow tube having a preliminary dropping device which forms a secondary Sprengel backing pump. The gases are discharged into a storage bulb which connects by way of a second stopcock with the vacuum line. On commencing to use the manometer, the entrance tube is fastened to the pump, both stopcocks are opened, and the liquid in manometer and boiling bulb are thoroughly degassed. Presently, the condensation pump starts operating and the column in the reference limb rises a little, indicating that a good vacuum has been secured. The alcohol boils merrily into the black radiator bulb. The stopcocks are now closed, and the gage transferred to its place of operation. The left-hand stopcock is opened and the gage becomes available for readings. It is always shut off under vacuum The reference side storage bulb should be re-evacuated every few days of continued use.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

THE DECOMPOSITION OF CITRIC ACID BY SULFURIC ACID

BY EDWIN O. WIIG[1]

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The effect of inhibitors on the decomposition of certain organic acids by sulfuric acid has been explained on the basis of the theory of negative catalysis proposed by Taylor,[2] who concluded from Lichty's study[3] of the retarding influence of water on the velocity of decomposition of oxalic acid that inhibitors functioned as negative catalysts by reducing, through molecular compound formation, the active mass of one or both of the reactants. Taylor's theory has been substantiated more or less by experimental investigations of the rate of decomposition of formic, malic, *o*-benzoylbenzoic and triphenylacetic acids in sulfuric acid by Schierz,[4] Whitford,[5] Gleason and Dougherty[6] and Dittmar,[7] respectively. However, the results obtained in these studies are not always in agreement with what might be expected on the basis of the theory. A study of the effect of inhibitors on the decomposition of citric acid by sulfuric acid was undertaken in the hope of clearing away some of the present inconsistencies and for the purpose of testing still further the theory of negative catalysis involved in these reactions.

The reaction between citric acid and sulfuric acid first was studied about 1839 by Robiquet,[8] who observed that on heating the two a gas was evolved which at first consisted of carbon monoxide and later of a mixture of that gas with carbon dioxide. Various workers investigated the reaction without throwing any light on it until, in 1884, it was finally explained by von Pechmann.[9] Sulfuric acid decomposes citric acid into carbon monoxide, water and acetone-dicarboxylic acid according to the equation

$$(CH_2COOH)_2C(OH)COOH \longrightarrow CO + H_2O + (CH_2COOH)_2CO$$

Acetone-dicarboxylic acid, which was isolated by von Pechmann, decomposes rather readily into acetone and carbon dioxide, so that its detection had escaped earlier investigators. Fortunately, the velocity of decomposition of acetone-dicarboxylic acid in sulfuric acid at the temperatures employed in the present research is extremely small compared to the rate at which citric acid decomposes. It was necessary to correct for the

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[1] National Research Fellow in Chemistry.

[2] Taylor, J. *Phys. Chem.*, *27*, 322 (1923).

[3] Bredig and Lichty, *Z. Elektrochem.*, 12, 459 (1906); Lichty, J. *Phys. Chem.*, 11, 225 (1907).

[4] Schierz, THIS JOURNAL, 45, 447 (1923).

[5] Whitford, *ibid.*, 47, 953 (1925).

[6] Gleason and Dougherty, *ibid.*, 51, 310 (1929).

[7] Dittmar, J. *Phys. Chem.*, 33, 533 (1929).

[8] Robiquet, *Ann.*, 30, 229 (1839).

[9] Von Pechmann, *Ber.*, 17, 2542 (1884).

carbon dioxide evolved from acetone-dicarboxylic acid in only three slow decompositions at 35°.

Experimental Part

Preparation and Purification of **Materials.**—U. S. P. citric acid was recrystallized from water three times and dried over calcium chloride in a desiccator. The resulting hydrated citric acid crystals melted at 153–154°, which agrees very well with the value of 153° given by Meyer.[10]

Four lots of sulfuric acid corresponding to 100.00, 100.44, 100.50 and 100.52% were used. These acids were prepared by mixing C. P. 95–96% sulfuric acid with Baker and Adamson's reagent 30% fuming sulfuric acid, and subsequently analyzed, using due precautions to prevent the loss of sulfur trioxide or the absorption of moisture, by titration with standard alkali and by precipitation as barium sulfate. Samples of the lot which analyzed 100.00% H_2SO_4 were found to have a melting point of 10.40°, which is in good agreement with the values obtained by previous investigators.[11] The acids containing excess sulfur trioxide were mixed with the calculated amount of 95.44% acid required to give exactly 100% sulfuric acid and the melting point of the resulting mixtures was found to be 10.42". Moreover, when used for the determination of the velocity constant at a particular concentration of acid, the various lots of acid gave concordant results. Sulfuric acid of any desired concentration between 95.44 and 100.52% was prepared by mixing the calculated quantities of the dilute and fuming acids. These acids were run out of burets filled by an all-glass siphoning system from ground glass-stoppered storage bottles. To replace the acid withdrawn, air was admitted into the storage bottles by aspiration through two bubbling bottles containing 100% sulfuric acid.

Apparatus and Method of Procedure.—The velocity of decomposition of citric acid in sulfuric acid was determined by observing the volume of carbon monoxide evolved at various times during an experiment. The reaction was carried out in 50-cc. round-bottomed pyrex flasks supported in a shaking device similar to that designed by Walton.[12] The agitator was so arranged that the flasks were immersed completely in a thermostat whose temperature was regulated to within ±0.02°. The thermometer employed was calibrated against a Bureau of Standards and a P. T. R. thermometer. Supersaturation of the reaction mixture with carbon monoxide was prevented by adding short pieces of glass rod to the flasks. Capillary tubing conducted the gas evolved to water-jacketed burets which were maintained at the same temperature as the thermostat.

The dilute and concentrated acids (total volume, 20 cc.) were run from their respective burets into the reaction flasks while the flasks were stoppered onto the buret; the pressure in the flasks was first slightly reduced so as to permit flow of the acid. The citric acid, contained in a glass capsule supported in the neck of the flask, could be dropped into the sulfuric acid when the latter had come to the temperature of the thermostat. In the preliminary experiments solid citric acid was used but the velocity constants obtained were not concordant, varying with the size of the citric acid particles and the volume of solvent. This difficulty was finally overcome by using a concentrated solution of citric acid in water (58.43% acid and 41.57% water). From 0.25 to 0.50 cc. of this solution (molality of citric acid in sulfuric acid = 0.027 to 0.052) was accurately measured out into the capsules from an arbitrarily calibrated microburet. Concordant results were then readily obtained. By varying the experimental procedure it was shown that the heat evolved on adding the aqueous solution of citric acid to the

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[10] Meyer, *Ber.*, 36,3599 (1903).

[11] Whitford, THIS JOURNAL, 47, 953 (1925).

[12] Walton, Z. *physik. Chem.*, 47, 185 (1904).

sulfuric acid had no effect on the reaction velocity. Later a solution of citric acid in approximately 80% sulfuric acid was used in order to eliminate any possibility of citric acid crystallizing before dissolving in the reaction mixture. Obviously, the water thus added with the citric acid was always included in calculating the strength of the sulfuric acid.

Results

Completeness and Order of Reaction.—In the preparation of acetonedicarboxylic acid by the decomposition of citric acid in fuming sulfuric acid yields of 92–97% have been reported.[13] The decompositions effected in this research always gave the theoretical yield of carbon monoxide within the limits of experimental error, except that in solutions containing more than about 0.5% sulfur trioxide the reaction is only about 80% complete. For example, four experiments at 25° in 96.46% H_2SO_4 gave an average of 46.65 cc. of carbon monoxide compared with the theoretical yield of 46.60 cc., while from four samples at 15° in 97.34% H_2SO_4 was evolved an average of 41.63 cc. compared with 41.70 cc. for quantitative decomposition. At the end of the experiments the sulfuric acid was nearly always colorless, indicating the absence of side reactions due to oxidation.

The decomposition of citric acid, although undoubtedly involving reaction with sulfuric acid, follows the unimolecular law. This was indicated by the "constancy" of the velocity constants obtained at various times in any one experiment as illustrated by the data given in Table I. That the velocity constants were independent of the rate of shaking was demonstrated by the use of four shaking speeds.

TABLE I

A TYPICAL EXPERIMENT

Temp., 35"; molality of H_2O, 1.67 (97.08% H_2SO_4); a = 42.4 cc.

t	x	$a - x$	$k \times 10^3$
2	7.8	34.6	102
4	14.2	28.2	102
6	19.2	23.2	100
8	23.4	19.0	100
10	26.8	15.6	100
12	29.4	13.0	99
14	31.7	10.7	98
16	33.4	9.0	97
22	37.3	5.1	96

At 50% decomposition $k \times 10^3 = 100$

The values of k in the above table were calculated by means of the equation for a unimolecular reaction

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

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[13] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 5

Volumes of carbon monoxide were substituted for concentrations of citric acid and the time t is in minutes. The concentration of water has been expressed in molality, *i. e.*, the number of moles of solute per 1000 g. of solvent.

It will be observed that the velocity constants in Table I fall off slightly. This is due to the water formed during the reaction, for at higher concentrations of sulfuric acid, where the reaction is much more sensitive to small amounts of water, the velocity constants decreased still more, while in more dilute solutions the values of k scarcely changed at all. The third product of the decomposition, acetone-dicarboxylic acid, may also contribute to the falling velocity constant. The addition of 0.047 molality acetone-dicarboxylic acid (equivalent to that formed during an experiment) to a reaction mixture containing 1.04 molality water changed $k \times 10^3$ from 78.2 to 65.3 at 25°, whereas an equal quantity of water would decrease $k \times 10^3$ to 67.7. Thus this acid appears to be fully as strong an inhibitor as water.

Independence of the velocity constant of the initial concentration of the reactant is another criterion of a unimolecular reaction. In 98.16% H_2SO_4 at 25° the average values of $k \times 10^3$ obtained with initial concentrations of citric acid of 0.051 and 0.027 molality were 77.2 and 80.5, respectively. The difference is small and almost within the limits of experimental error. The reaction is also apparently homogeneous since the addition of 5 g. of clean, dry sand to the reaction mixture had no effect.

The Effect of Water on the Reaction Rate.—In the hope of determining the mechanism of the inhibition by water and other substances, a

TABLE II

EFFECT OF WATER ON THE REACTION VELOCITY AT 15°

Water, %	Molality of water	$k \times 10^3$	Water, %	Molality of water	$k \times 10^3$
0	0	153	1.27	0.72	37.1
0.10	0.056	212	2.14	1.22	12.4
.19	.10	215	2.66	1.52	7.8
.26	.14	210	3.29	1.89	4.32
.39	.22	180	3.93	2.27	2.52
.68	.38	105	4.81	2.80	1.27
.81	.45	83.4			

TABLE III

EFFECT OF WATER ON THE REACTION VELOCITY AT 25°

Water, %	Molality of water	$k \times 10^3$	Water, %	Molality of water	$k \times 10^3$
0	0	440	1.27	0.72	156
0.052	0.029	630	1.84	1.04	78.2
.16	.09	740	2.41	1.37	41.5
.25	.14	795	2.97	1.70	25.0
.33	.18	760	3.54	2.03	15.4
.45	.25	650	4.44	2.58	7.2
.71	.40	387	5.23	3.07	4.16
1.00	.56	248			

TABLE IV

EFFECT OF WATER ON THE REACTION VELOCITY AT 35°

Water, %	Molality of water	k × 10^3	Water, %	Molality of water	k × 10^3
0	0	1210	1.18	0.66	690
0.10	0 056	1700	1.72	0.94	356
.19	.10	1940	2.42	1.38	157
.28	.16	2090	2.92	1.67	101
.40	22	2120	3.54	2.04	59.3
.50	28	1920	4.39	2.55	31.2
.70	.38	1360	5.18	3 03	17.5

study was made of the influence of water on the velocity of decomposition. The data obtained are summarized in Tables II, III and IV, and are represented graphically in Fig. 1. Each value of the velocity constant is the average of those obtained at 50% decomposition in from three to twelve experiments.

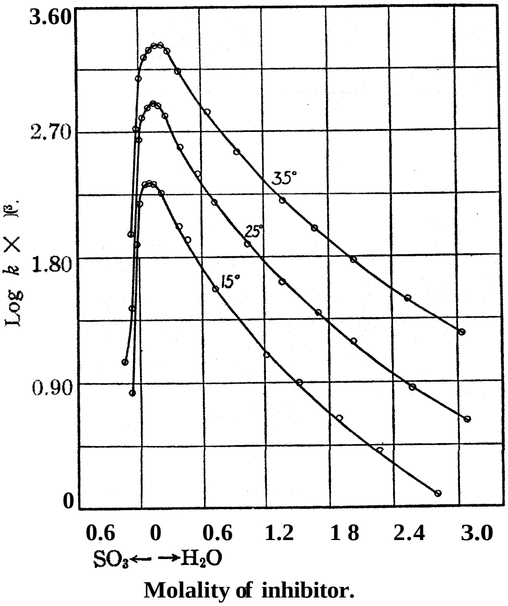

Fig. 1.—Effect of sulfur trioxide and of water on the reaction rate.

From the data it can readily be seen that small amounts of water in excess of a certain minimum concentration have a very marked retarding effect on the reaction rate, the relative effect decreasing as the concentration of water increases. Similar results have been obtained by previous investigators, particularly Lichty, who found the decomposition of oxalic acid to be even more sensitive to water.

The curves for the reaction rate at various concentrations of water at 15. 25 and 35° (Fig. 1) exhibit a maximum at molalities of about 0.10, 0.14 and 0.20, respectively. This entirely unexpected result has not been observed with the other acids that have been studied and was at first rejected as being due to the measurement of the rate of solution of citric acid in sulfuric acid instead of the rate of reaction. The work was repeated using, instead of a water solution of citric acid, an 80% sulfuric acid solution in which the decomposition at ordinary temperature is negligible. On dropping the capsule containing 0.7 cc. of this solution into 20 cc. of approximately 100% sulfuric acid there can be no crystallization or precipitation of the citric acid since the solubility[14] of citric acid in aqueous solutions of sulfuric acid reaches a minimum at approximately 60% acid and then increases with increase in sulfuric acid content. It was thought that possibly the maximum really corresponded to 100% sulfuric acid and that the analysis of the acid was incorrect, but a careful rechecking of the analysis gave the same result as found originally. Furthermore, the melting point of a sulfuric acid mixture made up exactly as in carrying out a decomposition in 100% sulfuric acid, except for the replacement of the aqueous citric acid solution by a carefully weighed equivalent amount of water, was 10.42°, corresponding to the melting point of 100% acid. In addition the velocity of decomposition of oxalic acid at 25° was measured in a 100% sulfuric acid solution made by mixing the calculated amounts of 100.50% and 95.44% acids. Since oxalic acid yields equal volumes of carbon monoxide and carbon dioxide, the gases were collected over a saturated magnesium sulfate solution which had been saturated with carbon dioxide at 25°. The average of three experiments gave $k \times 10^3 = 18.0$ at 50% decomposition. By interpolation the data of Lichty[15] give **17.4** and 12.0 for $k \times 10^3$ at 50% decomposition in 100% and 99.99% sulfuric acids, respectively. Thus the acid mixtures used in these experiments were in error, on the basis of Lichty's acids, by less than 0.01% sulfuric acid, which is much less than the error involved in analysis.

It was observed that the inhibiting effect of water might be decreased by the addition of another substance. At 25° in the presence of 0.56 molality water $k \times 10^3$ is 248. When only 0.032 molality anhydrous oxalic acid was added to such a mixture, $k \times 10^3$ became 260. Possibly the oxalic acid removes some of the water through hydrate formation.

The Effect of Sulfur Trioxide on the Reaction Rate.—Since Lichty[15] observed that the decomposition of oxalic acid proceeded more rapidly in a solution containing 1% excess sulfur trioxide than in 100% sulfuric acid, while Whitford[11] found that 1% free sulfur trioxide had no effect on the velocity of decomposition of malic acid and 12.5% decreased the rate to about 60% of that observed in 100% sulfuric acid, it was important to determine the effect of the free oxide in the case of citric acid. The data obtained are given in Table V and shown graphically in Fig. 1

TABLE V

EFFECT OF SULFUR TRIOXIDE ON THE REACTION RATE

		$k \times 10^3$		
SO_3, %	Molality of SO_3	15°	25°	35°
0	0	153	440	1210
0.27	0.034	78	...	530
.67	.084	6.8	27.4	94
1.15	.15	...	11.3	..

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[14] Knox and Richards, J. *Chem. Soc.*, 115, 520 (1919).

[15] Lichty, J. *Phys. Chem.*, 11, 225 (1907).

as a continuation of the curves for the effect of water. The marked inhibiting effect of sulfur trioxide, even greater than water, was rather unexpected but it fits in very well with the finding of the maximum discussed in the preceding section.

The Effect of Temperature on the Reaction Rate.—Schierz and Dittmar indicate that the temperature coefficients for the decomposition of formic and triphenylacetic acids change very irregularly with the concentration of the sulfuric acid. To show that these apparent irregularities are probably due to experimental error the temperature coefficients for the decomposition of citric acid have been calculated. The curves in Fig. 1 were plotted on a much larger scale and the value of the temperature coefficient at various molalities of water was readily obtained from the distance between two curves. From the integrated form

$$E = \frac{1.98\, T_2 \times T_1 \times 2.303 \log k_2/k_1}{T_2 - T_1}$$

of the Arrhenius equation expressing the relation between the absolute temperature and the reaction velocity constant, k, the "critical increment" or "energy of activation," E (in calories), was calculated. The results are shown in Table VI, where each value of the temperature coefficient is the average of those obtained from three separate sets of curves.

TABLE VI

TEMPERATURE COEFFICIENTS OF THE WATER INHIBITED REACTION

Molality of water	Temperature coefficient k_{25}/k_{15}	 k_{35}/k_{25}	"E" in calories 15–25'	 25–35'
0.4	3.92	3.53	23200	22900
.6	4.09	3.70	23900	23800
.8	4.29	3.70	24800	23800
1.0	4.30	3.76	24800	24100
1.2	4.31	3.81	24800	24300
1.4	4.27	3.86	24700	24600
1.6	4.29	3.92	24800	24800
2.0	4.32	3.92	24900	24800
2.2	4.31	4.03	24800	25300
2.4	4.29	4.09	24800	25600
2.6	4.34	4.13	24900	25800
2.8	4.41	4.12	25200	25700

A study of the table reveals the fact that for the same temperature interval the temperature coefficient increases as the amount of water increases, although several values are slightly less than that at the preceding smaller molality of water. These differences, however, are comparatively small and well within the limits of experimental error. Furthermore, it is very difficult to draw a smooth curve that will average the errors in all the experimental points. The large irregularities observed by the other investigators do not manifest themselves in this investigation; in fact, when the temperature coefficients for the decomposition of triphenylacetic acid are calculated as above from Dittmar's data, the same rather regular increase in temperature coefficient with increase of water is obtained. The value of the critical increment, theoretically, is practically a constant quantity for a given reaction and it is interesting to note that there is fairly good agreement between the two values of the activation energy at a given concentration of water.

Discussion

The decomposition of citric acid, as with the other organic acids investigated, is probably best explained by the assumption of an unstable sulfuric acid–citric acid complex. From a study of the solubility of citric acid in various concentrations of aqueous sulfuric acid, Knox and Richards[14] concluded that the two acids form a molecular compound. That the compound is sufficiently stable so that indications of its presence may be obtained might seem to be an argument against its playing a role in the decomposition of citric acid. However, in the aqueous solutions employed, the unstable citric acid–sulfuric acid complex is stabilized by water, which is a powerful inhibitor of the decomposition, possibly through hydration, of which the solubility measurements give no indication.

Whitford and Dittmar have pointed out that the velocity of decomposition in sulfuric acid of the organic acids already investigated is apparently related to the strength of the acid as measured by its acid dissociation constant. On this basis the rate of reaction in the case of citric acid should be less than for malic acid, whereas experimentally a considerably higher value is found. This would indicate that there are other factors besides acid strength to be taken into consideration.

Since in 100% sulfuric acid there undoubtedly exists the equilibrium[16] represented by the equation $H_2SO_4 \quad H_2O + SO_3$, and since sulfur trioxide was found to be a more powerful inhibiting agent than water, an explanation readily suggests itself for the maximum in the curves showing the effect of water. As successively smaller amounts of water are used the reaction mixture approaches 100% sulfuric acid and the velocity of decomposition increases until a point is reached at which there is sufficient dissociation of the sulfuric acid into sulfur trioxide so that the accelerating effect produced by decreasing the water content is more than offset by the stronger inhibiting influence of the sulfur trioxide, and the reaction rate decreases. In agreement with this explanation, the maximum in the curves in Fig. 1 is shifted in the proper direction by an increase in temperature.

The action of the inhibitors may be explained on the basis of Taylor's theory[2] of negative catalysis in which it is postulated that the added substance decreases the concentration of the active mass of one or more of

[16] Christiansen, *J. Phys. Chem*, **28**, 145 (1924); *Trans. Faraday Soc.*, **24**, 596 (1928)

the reactants through compound formation. In the present case water and sulfur trioxide would be assumed to form molecular complexes with either sulfuric acid or citric acid, or with both. Such compounds are, of course, well known.

The mechanism of inhibition in the decomposition of organic acids by sulfuric acid will be discussed in detail in a later paper.

The author takes great pleasure in acknowledging his indebtedness to Professor Hugh S. Taylor for his kindly interest in the problem and to Princeton University for supplying adequate facilities for its prosecution.

Summary

The decomposition of citric acid by sulfuric acid has been found to be quantitative and to follow the unimolecular reaction law.

Small amounts of water and of sulfur trioxide both have a pronounced inhibiting influence on the velocity of decomposition.

As the concentration of sulfuric acid was increased, the reaction rate increased until a maximum, varying with temperature, was reached; further removal of water decreased the rate. No such maximum has previously been reported.

For a ten degree rise of temperature the temperature coefficient is approximately 4, and it increases fairly regularly as the water content of the sulfuric acid is increased.

The decomposition is assumed to proceed through the formation of an unstable citric acid–sulfuric acid molecular complex. Inhibition by water and sulfur trioxide may be accounted for on the basis of Taylor's theory of negative catalysis.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

THE EFFECT OF SULFUR TRIOXIDE ON THE DECOMPOSITION OF OXALIC ACID BY SULFURIC ACID

BY EDWIN O. WIIG[1]

RECEIVED AUGUST 11, 1930 PUBLISHED DECEMBER 18, 1930

The effect of water, and certain other substances, on the decomposition of oxalic, formic, malic, o-benzoylbenzoic, triphenylacetic and citric acids[2] by sulfuric acid is to inhibit to a marked degree the velocity of reaction. This would indicate that the reaction mechanisms are analogous. There is one notable exception, however, in the similarity of the inhibiting effects of added materials. Lichty[2b] observed, qualitatively,

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[1] National Research Fellow in Chemistry.

[2] (a) Bredig and Lichty, *Z. Elektrochem.*, 12, 459 (1906); (b) Lichty, *J. Phys. Chem.*, 11, 225 (1907); (c) Schierz, THIS JOURNAL, 45, 447 (1923); (d) Whitford, *ibid.*, 47, 953 (1925); (e) Gleason and Dougherty, *ibid.*, 51, 310 (1929); (f) Dittmar. *J. Phys. Chem.*, 33, 533 (1929); (g) Wiig. THIS JOURNAL, 52, 4729 (1930).

that 1% of sulfur trioxide greatly increased the velocity of decomposition of oxalic acid whereas Whitford[2d] found 1% of sulfur trioxide to have no effect, while 12.5% decreased the reaction rate in the case of malic acid to about 60% of that observed in 100% sulfuric acid. In the decomposition of citric acid[zg] sulfur trioxide has a very marked inhibiting influence, much greater than water. It was pertinent, therefore, for the theories of negative catalysis involved in these reactions to determine quantitatively the effect of sulfur trioxide on the rate of decomposition of oxalic acid.

Apparatus and Materials

The velocity of decomposition of oxalic acid was followed by observing the volume of gas (carbon monoxide and dioxide) evolved at various times during an experiment. The apparatus and procedure employed were the same as in the previous investigation.[2g] The sulfuric acid mixtures were made up as before, except that those marked "approximate" in the data were prepared by mixing the calculated weights of 30% fuming and c. p. 96% acids. These mixtures may be in error by as much as 2% sulfur trioxide but are sufficiently accurate to indicate the trend of the velocity constants with change in acid concentration. The oxalic acid (Kahlbaum's "zur Analyse") was dissolved in 95% sulfuric acid, in which the decomposition is negligible, and 0.7 cc. of this solution used in an experiment. Where necessary the water thus added was taken into consideration in calculating the final sulfuric acid concentration.

Results

As Lichty has shown that the decomposition of oxalic acid follows the unimolecular law, the velocity constants were calculated by the usual equation. The data obtained at 15 and 25° are given in Table I, where

TABLE I

EFFECT OF SULFUR TRIOXIDE ON THE VELOCITY OF DECOMPOSITION OF OXALIC ACID BY SULFURIC ACID

Temp., °C.	SO_3, %	Molality of SO_3	$k \times 10^3$
25	0	0	18.0
	1.11	0.140	930
	1.47	.186	1050
	1.60	.203	1190
	4^a	.5	1800
	8"	1.1	1960
	14"	2.0	2040
	30^a	5.3	1960
15	4^a	0.5	1130
	8^a	1.1	1260
	14^a	2.0	1430
	30^a	5.3	1290

[a] Approximate composition.

each value is the average of $k \times 10^3$ at 50% decomposition obtained in three or four experiments. In 100% sulfuric acid $k \times 10^3$ is 18.0, which agrees very well with the value of 17.4 obtained by interpolation from Lichty's data. The results given in the table, together with the data of Lichty, are represented graphically in Fig. 1. For comparison part of the analogous curve for citric acid has been reproduced in the figure.

It will be observed that the rate of decomposition of oxalic acid in sulfuric acid increases with increase in sulfur trioxide until a maximum is reached in about 14% fuming acid, after which the rate falls off slightly. As the velocity of decomposition is extremely rapid at 25° ($t_{1/2}$ is of the order of one-third minute at 14% SO_3), a series of experiments was performed at 15° to confirm the maximum observed at 25°.

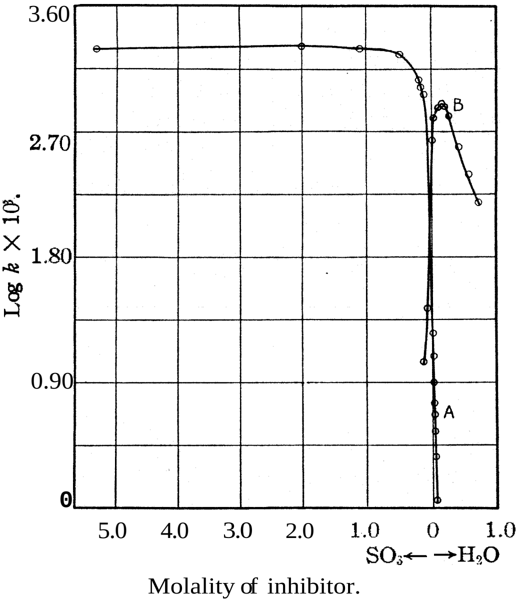

Fig. 1.—Effect of sulfur trioxide and of water on the reaction rates of oxalic and citric acids. A—oxalic; B—citric.

Discussion

The results obtained for the effect of sulfur trioxide on the decomposition of oxalic acid by sulfuric acid appear to conform with the analogous effects in the case of citric and malic acids. From the figure it may be seen that water has an extremely large inhibiting influence on the decomposition of oxalic acid while sulfur trioxide is a very weak inhibitor, as shown by the slight falling off in the velocity at a molality of 5.3. The increase in the reaction rate on increasing the sulfur trioxide molality from 0 to 2.0 may be attributed to a decrease in concentration of minute amounts of water formed by the thermal dissociation of sulfuric acid (H_2SO_4 $H_2O + SO_3$) rather than to an accelerating effect of sulfur trioxide. The slope of the curve for the effect of water on the oxalic acid decomposition would indicate the plausibility of such an assumption. An analogous explanation was given to account for the maximum in the citric acid curve. Christiansen[3] has previously pointed out that displacement of the equilibrium H_2SO_4 $SO_3 + H_2O$ may determine the rate at which oxalic acid decomposes, but he also sug-

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[3] Christiansen, J. *Phys. Chem.*, 28,145 (1924); *Trans. Faraday Soc.*, 24,596 (1928).

gests that the reaction actually measured may be between oxalic acid and SO_3 or some other "sulfuric acid" which is less hydrated than H_2SO_4.

If the equilibrium constant at 25° for the reaction H_2SO_4 H_2O + SO_3 were known, the concentration of water and of sulfur trioxide inhibiting, respectively, the oxalic and citric acid reactions in 100% sulfuric acid could be calculated. Fortunately there are sufficient data available in the literature so that such a calculation may be made.

Bodenstein and Katajama[4] have studied the thermal dissociation of sulfuric acid in the gas phase. From the empirical equation which they give for the variation of the equilibrium constant with temperature, K_c (in moles/liter) may be calculated for the constant boiling acid (317°).[5] Since the vapor and liquid of a constant boiling mixture have the same composition and since the liquid analyzes 98.54% H_2SO_4, the concentration of sulfur trioxide, water and sulfuric acid in the gas phase may be obtained. The same ratio must hold for the liquid, from which the composition of the mixture, expressed in molalities, is calculated to be $H_2O = 3.976$, $SO_3 = 2.815$, $H_2SO_4 = 10.20$. These data readily give K, expressed in molalities, for the liquid at 317'.

The equilibrium constant at 25° may now be calculated by means of the equation of the reaction isochore[6] $d \ln K/dT =$ AH/RT^2. To make use of the integrated form of this equation, it is necessary to know the heat of reaction and the specific heats of the substances involved over the temperature range 25–317°. From heats of formation,[7] the heat absorbed by the reaction $H_2SO_4(l) \longrightarrow H_2O(l) + SO_3(l)$ is found to be 20,290 calories at 18°. The known specific heats[S] (in joules/gram) are $H_2O(l) = 4.18–4.35$ from 20 to 300° and $H_2SO_4(l) = 1.42 + 0.0016t$ from 10 to 45°. The specific heat of $SO_3(l)$ was estimated to be about 1.40 from analogy with SO2 (= 1.37–1.43 from 20 to 40°) and from the similarity in specific heats of $H_2SO_4(l)$ and $H_2S_2O_7(l)$ (=1.4 at 35°). The values for the specific heats used in the calculations are $H_2O(l) = 4.18$, $H_2SO_4(l) = 1.45$, $SO_3(l) = 1.4$; these values are probably sufficiently accurate. At 25° the value $1.09 \text{ X } 10^{-8}$ was found for K. This gives for the water and sulfur trioxide concentrations[9]

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[4] Bodenstein and Katajama, Z. *Elektrochem.*. 15, 224 (1909).

[5] Tammann, Z. *anorg. Chem.*, 161, 363 (1927); Knietsch, *Ber.*, 34, 4069 (1901).

[6] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 613.

[7] "International Critical Tables," Vol. V, pp. 176–178.

[8] "International Critical Tables," Vol. V, pp. 106, 113, 114.

[9] The calculation is, of course, only approximate since it has been tacitly assumed that the molecular species in the gas and liquid phases of the constant-boiling mixture are the same and that 100% sulfuric acid at 25° is not polymerized. If these factors could be taken into consideration, smaller values for the concentrations of sulfur trioxide and of water in 100% sulfuric acid would be obtained. The indicated concentrations are therefore maxima but they show very well the tremendous influence of minute amounts of inhibitors.

in 100% sulfuric acid a molality of 3.3×10^{-4}, which corresponds to 0.0026% SO_3 and 0.0006% H_2O. The concentrations of the stronger of the two inhibitors at the maxima of the two curves must be still smaller. By extrapolating the curve for the effect of water on the citric acid reaction rate to zero water, $k \times 10^3$ is found to be about 1800. Thus 0.0026% SO_3 decreases $k \times 10^3$ from 1800 to 440 in the case of citric acid. On the assumption that sulfur trioxide is not an accelerator for the oxalic acid reaction but that water is the inhibitor, a concentration of 0.0006% water reduces $k \times 10^3$ from about 2000 to 18.

It is interesting to note that the maxima in the two curves correspond to a minimum and a maximum in electrical conductance. The maximum in the citric acid curve is at about 0.25% water while Knietsch[10] and Kohlrausch[11] found a maximum in electrical resistance for aqueous resistance for aqueous sulfuric acid solutions at 0.05–0.10 and 0.25–0.26% water, respectively. Similarly in fuming acids Knietsch found a minimum in electrical resistance at 14–16.7% sulfur trioxide whereas oxalic acid decomposes most rapidly at about 14% sulfur trioxide.

Inhibition in the decomposition of organic acids by sulfuric acid is best explained by Taylor's theory[12] of negative catalysis. The experimental results for the effect of sulfur trioxide on the oxalic, malic and citric acid reactions are shown by the present work to be in accord with that theory. A discussion of the application of Taylor's theory of negative catalysis to these reactions will be given in another paper.

The writer wishes to express his gratitude to Professor Hugh S. Taylor for his interest in the progress of the work.

Summary

The rate of decomposition of oxalic acid has been studied in sulfuric acid mixtures containing from 0 to 30% free sulfur trioxide. The maximum velocity is obtained at about 14% sulfur trioxide (2.0 molality).

The data have been interpreted to indicate that sulfur trioxide is not a positive catalyst for the reaction but merely decreases the concentration of water, which is a very powerful inhibitor, the sulfur trioxide in this case being a relatively weak inhibitor.

PRINCETON, NEW JERSEY

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[10] Knietsch, *Ber.*, 34, 4069 (1901).

[11] Kohlrausch, *Wied.* Ann., 17, 69 (1882).

[12] Taylor, J. *Phys. Chem.*, 27, 322 (1923).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

INHIBITION IN THE DECOMPOSITION OF ORGANIC ACIDS BY SULFURIC ACID

BY EDWIN O. WIIG[1]

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The most outstanding group of negative catalytic reactions in homogeneous solution to which Taylor's theory of negative catalysis appears to apply is probably that which deals with the decomposition of organic acids by sulfuric acid. The results of the first intensive study of inhibition in these reactions were published by Bredig and Lichty in 1906. Within the past few years, principally through the efforts of Professor Walton and his students at Wisconsin, several other reactions of this type have been investigated. There are now data available for the effect of inhibitors on the velocity of decomposition of six organic acids in sulfuric acid. In addition to the well-known investigation of Bredig and Lichty[2] on the decomposition of oxalic acid, studies have been made of the reaction of sulfuric acid with formic,[3] malic,[4] *o*-benzoylbenzoic,[5] triphenylacetic[6] and citric[7] acids. In addition, the influence of inhibitors on the temperature coefficient of the malic acid[8] reaction and the effect of sulfur trioxide on the decomposition of oxalic acid[9] have been measured. In view of the increasing interest in inhibited reactions in general, the data covering the decomposition of organic acids in sulfuric acid have been deemed sufficient to warrant an analysis of the experimental results, together with a discussion of the application, of Taylor's theory[10] of negative catalysis.

The decompositions mentioned above all follow the unimolecular reaction law in spite of the fact that sulfuric acid would seem to be one of the reactants. This may be due to the large excess of sulfuric acid always employed, since under such conditions the change in its concentration in a single experiment would be negligible. On the other hand, the reaction may be a true unimolecular decomposition if we consider that the reaction whose velocity is actually measured is the decomposition of a sulfuric acid–organic acid complex. The velocity constants obtained are not,

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[1] National Research Fellow in Chemistry.

[2] Bredig and Lichty, *Z. Elektrochem.*, 12, 459 (1906); Lichty, *J. Phys. Chem.*, 11, 225 (1907).

[3] Schierz, THIS JOURNAL, 45, 447 (1923).

[4] Whitford, *ibid.*, 47, 953 (1925).

[5] Gleason and Dougherty, *ibid.*, 51, 310 (1929).

[6] Dittmar, *J. Phys. Chem.*, 33, 533 (1929).

[7] Wiig, THIS JOURNAL, 52, 4729 (1930).

[8] Dittmar, *ibid.*, 52, 2746 (1930).

[9] Wiig, *ibid.*, 52, 4737 (1930).

[10] Taylor, *J. Phys. Chem.*, 27, 322 (1923).

however, always constant but often decrease considerably. As the reaction being studied always produces water or other inhibitors, a falling velocity constant is to be expected. The magnitude of the decrease in the velocity constant depends on the extent to which the substance formed inhibits. Thus, in the decomposition of oxalic acid[2] in 100% sulfuric acid at 25°, $k \times 10^3$ decreases from 21.5 to 11.9 during a single experiment. This is in agreement with the observation that water is an extremely powerful inhibitor of the reaction. In contrast with this, water is a comparatively weak inhibitor for the condensation of o-benzoylbenzoic acid and, as might be predicted, the water formed during the reaction does not cause a measurable decrease in the velocity constant. Furthermore, where a reaction displays sensitiveness to the small quantity of water formed during the experiment, this sensitiveness vanishes in the more dilute sulfuric acid solutions used.

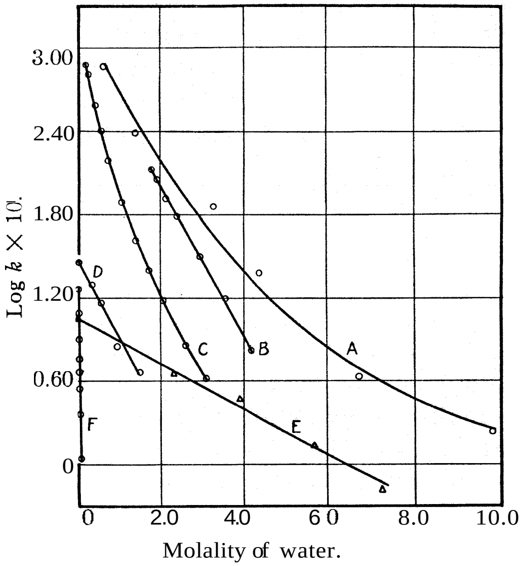

Fig. 1.—Effect of water on the reaction rates of (A) formic, (B) triphenylacetic, (C) citric, (D) malic, (E) *o*-benzoylbenzoic and (F) oxalic acids. A, C, F at 25°; B at 12°; D at 30"; E at 75°.

Inhibition by Water.—The effect of water on the velocity of decomposition of the six acids investigated has been determined over wide concentrations and at temperatures varying from 12 to 98°. In Fig. 1 there is presented one curve for each acid showing the influence of water on the reaction velocity at 25° or as near thereto as the data permit. The values used in plotting the curves are those given in the original papers except in the case of formic and o-benzoylbenzoic acids. For the former the velocity constants of Schierz[3] were multiplied by 2.303 to obtain the ordinary velocity constant, but, for the latter acid, velocity constants are given at only one concentration of sulfuric acid. Fortunately, Gleason and Dougherty[5] have presented their experimental data in the form of a curve showing the percentage of o-benzoylbenzoic acid decomposed at four hours as a function of the sulfuric acid concentration. By substituting in the usual equation for a unimolecular reaction $a = 1$, $t = 240$ and $x =$ the fraction of o-benzoylbenzoic acid condensed, we obtain one value of the velocity constant for each concentration of sulfuric acid. In view of the small inhibiting effect of water in this reaction, one value is sufficiently accurate for purposes of comparison.

From the figure it may be seen that in all six cases the effect of water is an exponential function of the concentration. Gleason and Dougherty[5] concluded that for o-benzoylbenzoic acid the retarding action of added water is in direct proportion to the amount added, and that it would appear that the o-benzoylbenzoic acid condensation differs fundamentally from reactions of the oxalic acid type. However, the curve for *o*-benzoylbenzoic acid in Fig. 1 indicates that the velocity constant is a logarithmic function of the added water and consequently this decomposition is similar to the others. Although these reactions are all of the same type, they differ in sensitivity to inhibition by water. The influence of water, as measured by the slope of the curves, is greatest in the decomposition of oxalic acid and least for o-benzoylbenzoic acid. At small concentrations of water the relative effect is nearly the same for the other four acids. The strength of the acids, as measured by the ordinary acid dissociation constants, decreases in the order oxalic, citric, malic, o-benzoylbenzoic, formic, triphenylacetic. Thus it may be seen that there is apparently no relationship between the strength of the acid undergoing decomposition and the retarding action of water. However, there may be some question as to whether it is justifiable to carry over into sulfuric acid, for purposes of comparison, dissociation constants that were determined with water as the solvent.[11]

Inhibition by Sulfur Trioxide.—The influence of sulfur trioxide on the rate of decomposition has been studied for only three of the six acids under consideration. For a number of years there was an apparent inconsistency in the results obtained with this substance. Bredig and Lichty[2] found qualitatively that 1% SO_3 accelerated the decomposition of oxalic acid to such an extent that it could not be measured by the method they employed. Whitford,[4] working with malic acid, found 1% SO_3 to have no effect while 12.5% decreased the reaction rate. Recently the effect of sulfur trioxide has been determined in the case of citric[7] and oxalic[8] acids and now the results appear entirely concordant. Figure 2 shows graphically the experimental results that have been obtained.

It will readily be seen that the three curves conform in shape to a curve with a maximum. The position of the maximum and the slopes of the curve on either side of the maximum depend wholly on the relative inhibiting powers of water and of sulfur trioxide. The relative retarding effects may be summarized as in Table I.

Since there exists in sulfuric acid the equilibrium $H_2SO_4 \quad H_2O + SO_3$ and since the ratio of the relative inhibiting powers of water and of sulfur trioxide may have any value whatever, the maximum reaction ve-

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[11] Kolthoff, *Rec. trav. chim.*, 49, 413 (1930).

TABLE I

INFLUENCE OF H_2O AND OF SO_3 ON THE REACTION KATE

Acid	Relative inhibiting power Water	 Sulfur trioxide
Oxalic	Very, very strong	Very weak
Malic	Strong	Weak
Citric	Strong	Very strong

locity may occur anywhere within a concentration range determined by the equilibrium. It may be predicted that when formic, triphenylacetir and *o*-benzoylbenzoic acids are studied over sufficiently great concentrations of water and of sulfur trioxide in sulfuric acid, a maximum analogous to those in Fig. 2 will be found in each case.

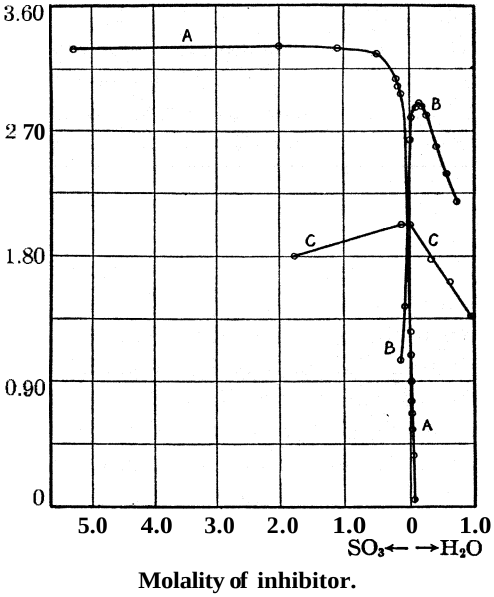

Fig. 2.—Effect of sulfur trioxide and of water on the reaction rates of (A) oxalic, (B) citric and (C) malic acids. A, B at 25°; C at 40°.

Relative Rates of Decomposition.—-Attempts have been made to find some relationship between the velocity of decomposition of the organic acids and their strength. For the acids studied up to 1925 Whitford[4] gives the following table, where the velocity constant is for the reaction in 0.562 molality of water at 50°.

Dittmar[6] added triphenylacetic acid to this list since he found that it decomposes more rapidly than formic acid and is the weakest acid of the four. Also, Dittmar points out that the reaction velocities increase in the order of decreasing heats of activation as calculated from temperature coefficients by means of the Arrhenius equation. An inspection of the curves in Figs. 1 and 2 shows that such comparisons no longer hold when all the data now available are considered. The decomposition velocities vary so greatly with the concentration of water and of sulfur

TABLE II

RELATION OF ACIDITY TO REACTION VELOCITY

Acid	Dissociation constant	Velocity constant
Oxalic	3.8×10^{-2}	0.515
Malic	4.0×10^{-4}	158.5
Formic	2.1×10^{-4}	Reaction immeasurably fast

trioxide that the organic acids might be arranged in several orders of increasing reaction rates.

The original comparison of Whitford was based on Kendall's rule[12] that the tendency toward molecular compound formation between sulfuric acid and an organic acid varies with the acidity of the second acid. The decomposition of the organic acids which have been investigated is supposed to proceed by way of an unstable sulfuric acid–organic acid complex, so that Kendall's rule should apply here *provided* the mere tendency toward compound formation can be assumed to govern the velocity of reaction. We have just seen, however, that reaction velocity comparisons cannot be made (unless an extrapolated value for each acid in the total absence of inhibitors can be obtained). Furthermore, Kendall's rule is at the best qualitative. For example, Hoogewerf and van Dorp[13] isolated an addition compound of sulfuric acid with mesaconic acid ($K_A \times 10^4 = 8$), whereas Kendall and Carpenter[12] obtained no indication by the freezing point method of similar compound formation between sulfuric acid and α-chlorocrotonic acid ($K_A \times 10^4 = 7.2$). The structure of the organic acid, the presence of various groupings, steric hindrance, etc., may play a not inconsiderable role in molecular compound formation. In addition, as already mentioned, acid dissociation constants determined in water solution may not furnish a proper basis of comparison when the medium is sulfuric acid. It is not surprising, therefore, to find that there is no apparent relation between velocity of decomposition and the ordinary acid dissociation constant of the organic acids. Furthermore, no such relationship would be expected since the rate of decomposition of the organic acid-sulfuric acid complex would depend on its instability rather than the rate or extent of its formation.

The Effect of Miscellaneous Inhibitors.—The retarding influence of numerous substances other than water and sulfur trioxide has been studied. Whitford[4] and Dittmar[6] found, in agreement with Kendall's rule for compound formation, that sodium and potassium sulfates were stronger inhibitors than water for the decomposition of malic and triphenylacetic acids. However, in the case of oxalic acid, Bredig and Lichty[2] found that water was a slightly better inhibitor than potassium sulfate. Dittmar's data covering the effect of a large number of inhibitors on the velocity of decomposition of malic and triphenylacetic acids show analogous differences very convincingly. For example, ethyl alcohol is a better inhibitor than crotonic acid in the decomposition of triphenylacetic acid but the reverse is true in the case of malic acid. A similar relationship holds for the following pairs of inhibitors: phenol–*p*-cresol, ethyl alcohol–*o*-toluic acid, coumarin–o-toluic acid, benzophenone–o-toluic acid.

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[12] Kendall and Carpenter, THIS JOURNAL, 36, 2506 (1914).

[13] Hoogewerf and van Dorp, *Rec. trav. chim.*, **18**, 211 (1899).

These results are not unexpected when we recall the wide variation in the relative effects of water and of sulfur trioxide on the decomposition of oxalic, malic and citric acids. If the action of an inhibitor depended solely on compound formation with sulfuric acid, then the same relative effects on the velocity of decomposition of the organic acids by sulfuric acid should be obtained. Since the experimental results show such marked differences in inhibiting power, it must be concluded that it is not sufficient to consider only the tendency toward compound formation with sulfuric acid in seeking for a mechanism of inhibition. In this connection Dittmar[5] points out that although phosphoric acid is an inhibitor for the decomposition of malic and triphenylacetic acids, no molecular compound of phosphoric and sulfuric acids has been shown to exist. On the other hand, Walton and Kepfer[14] have found, from solubility measurements, that phosphoric acid forms a molecular complex with malic acid. Dittmar concludes, therefore, that inhibition may be more satisfactorily explained by compound formation between malic acid and the inhibitor.

The Effect of Temperature.—Determinations of temperature coefficients have been made for the six organic acids whose decompositions have been studied but many of the values vary so much that they are not of much use for purposes of comparison. The chance for error is so large in these sulfuric acid systems that only by making careful measurements at a large number of sulfuric acid concentrations at two or more temperatures can dependable values of the temperature coefficient be obtained. In this way the experimental errors may be averaged, but in much of the data given in the literature this has not been taken into consideration. However, it may be stated that, in general, the addition of an inhibitor increases the temperature coefficient, and increase in concentration of the inhibitor increases the temperature coefficient. Where there are exceptions to these statements, and there are several, more data are usually needed before a definite decision may be made.

Dittmar[5] has determined the temperature coefficients for the decomposition of malic acid by sulfuric acid in the presence of a large number of inhibitors and finds that, in general, the temperature coefficient is greater than that for 100% sulfuric acid. Also, in the majority of the experiments the temperature coefficients increase with increase in inhibitor concentration. This last generalization holds very well for citric acid[7] also, where the data for the effect of water are sufficiently complete so that the trend of the temperature coefficient may be seen. The results are thus in general agreement with Dhar's[15] statement that a negative catalyst increases the temperature coefficient of a reaction. In the event

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[14] Walton and Kepfer, J. *Phys. Chem.*, 34, 543 (1930).

[15] Dhar, *ibid.*, 28, 951 (1924).

that these reactions follow a chain mechanism, the agreement with Dahr's rule may be only fortuitous, since at present the temperature coefficient of a chain reaction has no theoretical significance.

Mechanisms

Of the Decomposition.—It is rather generally agreed that the decomposition of oxalic, formic, malic, triphenylacetic, o-benzoylbenzoic and citric acids is brought about by the formation of an unstable sulfuric acid–organic acid complex (oxonium compound) which subsequently breaks up into the reaction products and sulfuric acid. The process may be represented by the equations

$$\text{Organic Acid} + H_2SO_4 \rightleftharpoons \text{Organic Acid}\cdot H_2SO_4 \quad (1)$$

$$\text{Organic Acid}\cdot H_2SO_4 \longrightarrow \text{Products of decomposition} + H_2SO_4 \quad (2)$$

The experimentally determined velocity would be that of the second reaction, which is dependent on the concentration of the molecular complex. Thus, it is evident that these reactions are not to be considered as simple dehydrations. This is convincingly shown by the fact that the decomposition of triphenylacetic acid by sulfuric acid involves no water at all, the products being triphenylcarbinol and carbon monoxide.

There is also the possibility that the formation of the simple organic acid–sulfuric acid complex is not in itself sufficient for decomposition, especially in view of the fact that evidence for the existence of these compounds has been obtained in the case of oxalic, citric and malic acids from solubility data. It may he that addition of another molecule of sulfuric acid at a second point in the organic acid (which is possible since the acids all contain two or more oxygen atoms) is required to produce sufficient strain to cause a rupture of the atomic linkages. This process would also give a unimolecular reaction. The effect of inhibitors would be the same in the two cases. However, this mechanism really has nothing to recommend it as being better than the simpler one given first. Moreover, the data which indicate compound formation of oxalic,[16] malic[8] and citric[16] acids with sulfuric acid have been obtained in aqueous solutions where it is quite possible that these molecular compounds are also combined with water, a possibility of which the method employed can give no evidence.

Of Inhibition.—The retardation of the velocity of decomposition of organic acids in sulfuric acid by the addition of a third substance may best be explained by what has come to be known as Taylor's theory[10] of negative catalysis. The Titoff concept, according to which a negative catalyst acts by suppression of a positive catalyst, certainly does not hold for these reactions, especially when one considers the positions of the maxima in the curves for citric, malic and oxalic acids in Fig. 2. Like-

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[16] Knox and Richards, *J. Chem. Soc.*, 115,508 (1919)

wise, as pointed out by Christiansen[17] for the decomposition of oxalic acid in sulfuric acid, the chain reaction theory does not appear to be applicable to these inhibited decompositions, though there is no direct experimental evidence on which to base such a conclusion. That chain reactions may occur in solution is shown by the work of Bäckström[18] and of Alyea and Bäckström[19] on the oxidation of sodium sulfite solutions. The reaction between mercuric chloride and the oxalate ion in aqueous solution also appears to be a chain reaction.[20] It is not impossible, therefore, that the decomposition of organic acids in sulfuric acid may be chain reactions.

Deactivation by mere collision of the inhibitor with organic acid–sulfuric acid complexes which have acquired sufficient energy to undergo reaction also seems to be out of the question. In this case inhibition would depend only on the number of free molecules of the negative catalyst. At a given concentration of inhibitor, then, approximately the same relative decrease in the velocity of decomposition should be observed for all the acids whereas the actual effect. vary greatly. This difficulty might be obviated by assuming a specific deactivating effect for each molecular complex, but then we really approach momentary compound formation instead of mere physical impact.

The mechanism of negative catalysis proposed by Taylor[m] is the direct opposite of that for positive catalysis in homogeneous reactions in solution where the reaction proceeds more readily by way of the intermediate compound, In negative catalysis the intermediate compound diverts one or more of the reactants from the main reaction, thus decreasing the active concentration of the reactants and slowing down the reaction velocity. According to the theory the function of inhibitors must be, in the present case, to bring about a decrease in the concentration of the unstable critical complex-organic acid·H_2SO_4. The concentration of the unstable complex is determined by the equilibrium represented in Equation 1. Consequently, its concentration may be reduced by a decrease in the concentration of (1) H_2SO_4, through the formation of H_2SO_4·Inhibitor, and (2) the organic acid, through the formation of Organic Acid·Inhibitor. A third possibility is that the active concentration of the complex, Organic Acid·H_2SO_4, may also be lowered by reaction of the addition compound itself with the inhibitor. It is evident then that inhibition may be brought about by any one, or various combinations, of the above three possibilities. However, by a consideration of the experimental data some of these mechanisms would seem to be eliminated.

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[17] Christiansen, *J. Phys. Chem.*, 28, 145 (1924); *Tmns. Faraday Soc.*, 24, 596 (1928).

[18] Backstrom, This Journal, 49,1460 (1927).

[19] Alyea and Bäckström, *ibid.*, 51, 90 (1929).

[20] Roseveare and Olson, *ibid.*, 51, 1716 (1929); Roseveare, ibid., 52,2612 (1930).

(a) Inhibition Due only to H_2SO_4 + Inhibitor $H_2SO_4 \cdot$Inhibitor.—That this possibility must be discarded has already been shown by the discussion in the section dealing with the effects of miscellaneous inhibitors. In case of inhibition by sulfur trioxide, for example, if compound formation with sulfuric acid were the only factor, then the effects with oxalic, malic and citric acids should be similar. Experimentally it is found that for the decomposition of citric acid sulfur trioxide is a very strong inhibitor, in the malic acid reaction a fair inhibitor, and for the oxalic acid decomposition an extremely weak inhibitor only after the concentration exceeds 14% SO_3.

(b) Inhibition Due only to Organic Acid + Inhibitor Organic Acid·Inhibitor.—The same sort of argument that was used to eliminate the preceding mechanism would appear to apply here. Kendall's rule for compound formation seems to work fairly well for hydrates of the acids but the inhibiting effect of water does not vary with the strength of the organic acid, as has previously been indicated. Similarly the very diverse effects of sulfur trioxide on the oxalic, malic and citric acid reactions seem to preclude the possibility that compound formation between the inhibitor and the organic acid determines completely the retarding action. Furthermore, Dittmar[5] found that o-toluic acid is a better inhibitor for the malic acid reaction than phosphoric acid, which has been shown to form a compound with malic acid, whereas compound formation between malic and o-toluic acids is scarcely to be expected since they are of nearly the same acid strength ($K_A \times 10^4$ is 4.0 and 1.25, respectively). While it would seem that compound formation between the organic acid and the inhibitor cannot be the only factor governing inhibition, still it must be admitted that there are weaknesses inherent in the reasons just advanced. Part of the argument depends on the use of the ordinary dissociation constants of the acids but the comparisons are made for sulfuric acid as the solvent, instead of water. Again, the effect of an inhibitor, o-toluic acid for example, in 100% sulfuric acid might be to change the H_2SO_4 $H_2O + SO_3$ equilibrium (by combination with either of the products). Then inhibition by o-toluic acid might be due to compound formation between water (or sulfur trioxide) and malic acid rather than between *o*-toluic and malic acids as we have supposed. However, the mechanism being discussed would seem to be eliminated definitely by the consideration, in the next section, of the extremely small concentrations of negative catalysts necessary for inhibition to manifest itself.

(c) Inhibition Due to Reaction of the Inhibitor with the Organic Acid·Sulfuric Acid Complex.—This postulate is so flexible that no experimental evidence may be adduced against it. If it be assumed that reaction of the negative catalyst with the fugitive complex is highly specific, then this mechanism must be in agreement with the observed effects for all the negative catalysts. Since the acid properties of the two acids in the oxonium addition compound are very probably altered, the assumption of specific inhibitor effects is reasonable.

There are several experimental facts that would seem to be in accord with this mechanism. The concentration of the critical complex must, of course, be very small, so that inhibition by very minute amounts of negative catalysts should be possible. Such inhibition is indicated in the case of oxalic and citric acids. It will be recalled that for citric acid[7] the maximum reaction velocity at 25° occurs at 0.14 molality of water (0.25%). The decrease in the velocity of decomposition at concentrations of water less than 0.14 molality was attributed to the presence of sulfur trioxide formed as a result of the reaction $H_2SO_4 \quad H_2O + SO_3$. The concentration of sulfur trioxide in 99.75% sulfuric acid must be vanishingly small since calculations[9] indicate that its concentration in 100% sulfuric acid is at the most of the order of 3×10^{-4} molality. An entirely analogous explanation holds for the finding of the maximum reaction velocity for oxalic acid[S] at a molality of sulfur trioxide of about 2.0. If inhibition is due to compound formation with the sulfuric acid or the organic acid, or even both, it is difficult to see how a concentration of inhibitor of the order of 10^{-4} molality can influence the concentration of the organic acid-sulfuric acid complex simply by diverting an extremely minute amount of sulfuric acid or organic acid from the main reaction. Even in higher concentrations of water, say **3.0** molality, the concentration of free water, resulting from the equilibrium $H_2SO_4 + H_2O \leftharpoondown H_2SO_4 \cdot H_2O$, must be small, so that inhibition by reaction of this free water with the fugitive complex would not be sufficient to bring the reaction to a full stop.

We may, of course, have all three inhibiting mechanisms operative at the same time, especially in the more concentrated inhibitor solutions. It would appear from the foregoing discussion, however, that the negative catalytic action must be due principally to reaction of the inhibitor with the intermediate compound through which the decomposition proceeds. The only weakness in this mechanism is that its great flexibility makes it very difficult to devise experimental tests.

In view of the present lack of any positive evidence for the existence of reaction chains in the decomposition of organic acids in sulfuric acid, it would seem that Taylor's theory of negative catalysis offers the only satisfactory explanation for the effect of inhibitors on these reactions. It is well to bear in mind, however, that no definite decision with respect to the applicability of the chain reaction theory can be made until more data are available.

In conclusion, the author wishes to acknowledge his indebtedness to Professor Hugh S. Taylor for valuable suggestions and criticisms.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, THE TRAVELERS INDEMNITY COMPANY AND THE TRAVELERS INSURANCE COMPANY]

DETERMINATION OF MAGNESIUM WITH 8-HYDROXYQUINOLINE – GRAVIMETRICALLY, VOLUMETRICALLY AND COLORIMETRICALLY

BY W. A. HOUGH AND J. B. FICKLEN

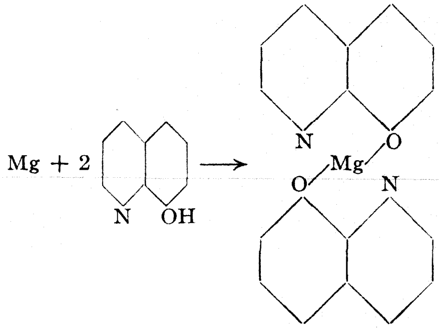
RECEIVED AUGUST 16, 1930 PUBLISHED DECEMBER 18, 1930

In an attempt to develop a quick method for the determination of magnesium in dilute solutions, particularly in boiler feed water analyses, the quantitative reaction which takes place in alkaline solution between the magnesium ion and a molar equivalent of 8-hydroxyquinoline with the formation of a light green precipitate was used.

Strebinger and Reif filtered off this salt through a Pregl filter tube, dried it at 105° for twenty minutes, and weighed it as $Mg(C_9H_6ON)_2 2H_2O$.[1]

The following methods diverge from that of Strebinger and Reif beyond the point where the green magnesium salt of 8-hydroxyquinoline is precipitated.

The reaction which takes place between the magnesium ion and 8-hydroxyquinoline is as follows



One part by weight of magnesium reacts with 11.9 parts by weight of 8-hydroxyquinoline.

An accurate standard solution of a magnesium salt which contained 0.1 gram of magnesium per liter was prepared.

The solution of 8-hydroxyquinoline was prepared by dissolving 0.5 g. in 100 cc. of alcohol and diluting to 1 liter. The solution obtained is of a bright yellow color.[2]

I. Gravimetric Method (**N. B.** Calcium must first be precipitated as oxalate and filtered off).—Take a sample containing at least 0.001 g. of magnesium and bring this sample to a volume of from 50 to 150 cc. Make ammoniacal with 20 cc. of ammonia reagent. Heat to 70° and add 100

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[1] Strebinger and Reif, *Chemical Abstracts*, 24, 2397 (1930).

[2] Allen, "Commercial *Organic Analysis*," Vol. *V*, p. 657.

cc. of a solution of 8-hydroxyquinoline containing 0.5 of this salt per liter. If the amount of magnesium present exceeds 0.004 g., add a larger amount of 8-hydroxyquinoline solution for completeness of precipitation, and, if necessary, add more 8-hydroxyquinoline. An excess of 8-hydroxyquinoline is made evident by the yellow color in the filtrate. Wash the precipitate with a weak solution of ammonium hydroxide, ignite strongly for thirty minutes in a porcelain crucible, and weigh as magnesium oxide.

Various amounts of the standard magnesium solution from 10 cc. (0.0010 g.) to 75 cc. (0.0075 g.) were run as above, and the actual results varied slightly from the theoretical. On the higher ranges the agreement was highly satisfactory. On the lower ranges the slight inaccuracies were due to the limitations inherent in the gravimetric method—such as error in weighing and taring, loss through slight solubility of the salt, loss through escape during ignition, and possible variance in the tare of filter paper ash.

Amounts of magnesium less than 0.0010 g. are not determined to good advantage gravimetrically, on account of the magnification of the above mentioned errors in consequence of the small quantity of magnesium present.

The table shows how results obtained compared with the theoretical.

TABLE I

COMPARISON OF RESULTS

Mg taken, mg.........	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	7.5	10.0
Mg found, mg.........	1.1	1.7	2.3	2.7	3.1	3.3	3.9	4.3	5.0	7.5	9.9

Magnesium taken as solution containing 0.1 mg. per cc.

II. Volumetric Methods.—Reagents: Solution of potassium permanganate, 4.17 g. per liter; N sulfuric acid. Precipitate the magnesium salt as described above, and wash with ammonium hydroxide. Dissolve the precipitate in 100 cc. of hot N sulfuric acid by immersing filter paper and precipitate in the acid and stirring. Titrate against the potassium permanganate solution until the pink color persists for two minutes. When the end-point is approached, the permanganate solution should be added, 0.5 cc. at a time, and the fading timed with a watch. Each cubic centimeter of potassium permanganate solution used is equivalent to 0.0001 g. of magnesium.

Various amounts of the standard magnesium solution from 1 cc. (0.0001 g. of magnesium) to 50 cc. (0.0050 g. of magnesium) were run, and up to 0.0025 g. of magnesium the results were very accurate. Larger amounts of magnesium than 0.0025 g. caused the end-point to be obscured by colored oxidation products imparting a brown color to the solution. Magnesium in amounts up to 0.0025 g. is determined to very good advantage by this method. In amounts larger than this, the gravimetric method is preferable. Of course, the sample can be diluted and an aliquot taken in order to bring the amount of magnesium into the effective range if it is too high to work to good advantage volumetrically. The table shows how results obtained compared with the theoretical.

TABLE II

COMPARISON OF RESULTS

Each milligram of magnesium taken represents 10 cc. of sample; each milligram found represents 10 cc. of potassium permanganate solution

Mg taken, mg.	0.10	0.20	0.30	0.40	0 50	0.80	1.00	1.20	1.40
Mg found, mg.	.14	.20	.33	.41	.48	.80	0.98	1.17	1.36
Mg taken, mg.	1.60	1.80	2.00	2.50	3.00	3.50	4.00	4.50	5.00
Mg found, mg.	1.60	1.84	2.03	2.55	3.16	3.75	4 45	5.05	5 75

III. Colorimetric Method.—The sample should not be of greater volume than 50 cc. Make alkaline with 20 cc. of ammonia reagent and add exactly 60 cc. of a solution of 8-hydroxyquinoline. (This latter solution should be prepared quantitatively.) Filter and wash with a small amount of weak ammonia. Make the volume of the filtrate up to 150 cc. with distilled water. The depth of color in the filtrate, due to the uncombined 8-hydroxyquinoline, is inversely proportinoal to the amount of magnesium in the sample. This can be compared in a 100-cc. colorimeter, using the 8-hydroxyquinoline solution as a standard. Since 1 cc. of 8-hydroxyquinoline solution is equivalent to 0.0000416 g. of magnesium, the following calculation can be made

$$\left(60 - \frac{3 \times \text{Reading}}{2}\right) \times 0.0000416 \times \frac{1{,}000{,}000}{\text{vol. of sample (cc.)}} = \frac{\text{parts of magnesium}}{\text{per million}}$$

Or if a 50 cc. sample is taken, which does not contain more than 50 parts of magnesium per million, this may be written in the form

$$1.248 \times (40 - \text{Reading}) = \text{parts of magnesium, per million}$$
$$49.92 - (1.248 \text{ X Reading}) = \text{parts of magnesium, per million}$$

If the amount of magnesium is greater than 50 parts per million, a correspondingly smaller sample should be taken and calculation made on the basis of the reduced sample. (The use of a sample containing a greater amount of magnesium than this makes necessary the use of a larger amount of 8-hydroxyquinoline solution, and is not advisable for reasons of economy.)

A range of amounts from 0.0005 to 0.0050 g. of magnesium were run as described above, and the results are shown herewith, as compared to the theoretical.

TABLE III

COMPARISON OF RESULTS

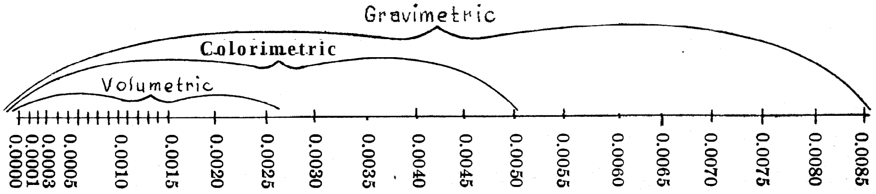
	8-Hydroxyquinoline							
	60 cc *used*					120 *cc. used*		
Mg taken, mg.	0.5	1.0	1.5	2.0	2.5	3 0	4 0	5 0
Reading.	28	24	18	10	5	18	9	4
Mg found, mg.	0.7	0.9	1.4	1.8	2.3	3.1	4.3	5.3

Summary

1. Quick determinations of magnesium can be made by precipitating it as the salt of 8-hydroxyquinoline and estimating the magnesium content of the salt either gravimetrically, volumetrically or colorimetrically. In many cases where the saving of time is an important factor and extreme accuracy is secondary, one of these methods may prove useful.

2. The most advantageous method to use depends on the amount of magnesium in the sample. (a) For amounts ranging from 0.0010 g. up to the highest concentrations, the gravimetric method is most accurate. (b) For amounts ranging from a minute trace up to 0.0025 g. the volumetric method is most accurate, and is very quick in comparison with many methods commonly used. (c) For amounts ranging from 0.0005 g. up to high concentrations (if proper aliquots are taken), the colorimetric method is very accurate and is the quickest of the three methods.

3. The following scale will illustrate at a glance the advantageous range of the three methods.



4. None of the other metals commonly found in natural waters will react with 8-hydroxyquinoline, except calcium.

HARTFORD, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE EMISSION SPECTRA OF SOME SIMPLE BENZENE DERIVATIVES

BY J. B. AUSTIN[1] AND IAN ARMSTRONG BLACK[2]

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The main features of the spectra obtained from the vapor of benzene and its simple derivatives under the excitation of the Tesla discharge have been described by McVicker, Marsh and Stewart,[3] who designated them as Tesla luminescence spectra to distinguish them from the fluorescence and absorption spectra. The present investigation was undertaken as an extension of this work; it was hoped on the purely chemical side to develop the suggestion made by them that a means of ascer-

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[1] From a dissertation presented by J. B. Austin to the Graduate School of Yale University, June, **1928,** in candidacy for the degree of Doctor of Philosophy.

[2] Commonwealth Fellow **1926–1928.**

[3] McVicker, Marsh and Stewart, J. *Chem. Soc.*, **123,642,2147 (1923).**

taining the purity of an organic solvent, and the nature of any impurities present, could be elaborated. In this respect it has been shown that such a method is unwieldy in practice, except perhaps for routine work in which a large number of samples are to be tested. Its application to a qualitive analysis would be relatively simple since a mere comparison of the unknown spectrum with a series of spectra of suspected impurities would suffice, but unfortunately the number of substances which yield satisfactory spectra under this means of excitation is rather limited. For a quantitative estimation of the amounts of impurities present it is necessary to compare the intensities of the bands, a procedure which is rendered difficult by the presence of a continuous background in many of the spectra.

On the other hand, it was thought that more comprehensive data on such spectra could be obtained which, with an increased accuracy, might enable the regularities observed in the bands to be given some theoretical interpretation. In this object some success has been achieved. A great many new band heads have been recorded with an accuracy believed to be ±0.5 Å. or better, except in the case of the faintest and most diffuse bands.

The spectrum of benzene appears to be unique among the substances thus far investigated in that it possesses an unusual completeness, its bands are very sharp and there is little if any continuous background. Because of these features it has been given special attention and has been discussed in a previous paper.[4] The present paper describes the spectra of toluene, ethylbenzene and the xylenes.

It was our original intention to extend this work to some of the aliphatic compounds but all the substances investigated, including pentane, 2,2,4-trimethylpentane and acetylene gave unsatisfactory results. The molecules broke down into fragments yielding spectra similar to those obtained with the electrodeless discharge. These have been described elsewhere.[5]

Experimental

Each hydrocarbon was shaken with concd. sulfuric acid until no color was imparted to fresh acid; it was then washed successively with concd. sodium hydroxide, dilute sodium hydroxide and distilled water until the final wash water was neutral to litmus. The resulting product was dried over sodium and distilled. The several boiling points were as follows:

Toluene	110–111° at 758 mm.
o-Xylene	142–142 5° at 750 mm.
m-Xylene	137–138° at 750 mm.
p-Xylene	136–137° at 750 mm.
Ethylbenzene	136–137° at 770 mm.

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[4] Austin and Black, *Phys. Rev.*, 35,452 (1930).

[5] Austin, THIS JOURNAL, 52, 3026 (1930).

The materials as finally used appeared to be quite pure and were at least free from each other, since in no case did the spectrum of any one contain the spectrum of any other.

The apparatus used in obtaining and measuring these spectra is described in detail in our paper on benzene. In each instance the pressure of the vapor was of the same order of magnitude as that used in the benzene study, being about 0.05 mm. Various vacuum waxes and cements were used in sealing the window on the discharge tube but no difference in the spectrum was observed A Hilger size C quartz spectrograph, giving a photograph 200 mm. in length for the range 2100 to 7000 Å. was used throughout, with exposures ranging from three to twelve hours. Since the resolution of this instrument was not very great the lines in the bands were not resolved, therefore most of the bands appeared as band heads shading off toward the red. The measurements given in Tables I to V were made on the heads of these bands.

Results

The first column in Tables I to V gives the wave lengths of the band heads in Ångström units as measured by us, the second column those of McVicker, Marsh and Stewart and the third column our values expressed as wave numbers in cm.$^{-1}$ ($\nu = 1/\lambda$). Our values are in general in agreement with those of McVicker, Marsh and Stewart, in most cases the differences being within their limit of error.

TABLE I

TESLA LUMINESCENCE BANDS OF TOLUENE

λ in Å., Austin and Black	λ in Å., McVicker, Marsh and Stewart	ν in cm.$^{-1}$ ($\nu = 1/\lambda$) Austin and Black
2667.5	2667	37477
2672.0	2671	37414
2680.2	2680	37300
2684.3		37243
2687.7	2688	37196
2692.5	2693	37129
2705.0	2705	36958
2713.0	2713	36849
2717.8	2718	36784
2724.9	2725	36688
2733.6	2733	36571
2741.1	2742	36471
2756.9	2755	36262
2771.2	2771	36075
2802.3	2804	35674
2818.6	2820	35468
2834.4	2834	35270
2884.3		34660
2896.3		34517

TABLE II

TESLA LUMINESCENCE BANDS OF *o*-XYLENE

λ in Å., Austin and Black	λ in, A., McVicker Marsh and Stewart	ν in cm.$^{-1}$ ($\nu = 1/\lambda$), Austin and Black
2679.1	2681	37315
2684.2	2686	37244
2688.5	2691	37184
2693.4		37117
2700.3		37022
2733.1	2736	36578
2738.3	2740	36508
2742.5		36452
2747.3		36389
2758.8		36237
2764.0		36169
2769.0		36103
2773.3		36048
2775.7		36016
2783.0		35922

Table I gives the data for the bands in the toluene spectrum, which contains, beside the bands, a continuous background starting sharply at A2667 and gradually shading out at about λ3100. The bands seem to be related in much the same way as are those of benzene but do not show the division into groups which is so evident in the latter.

The data for o-xylene are found in Table II. In this case the heavy background is the most prominent feature of the spectrum. It neither starts nor ends sharply but extends from about 12700 to 13300. No band groupings are apparent as with the other substances.

m-Xylene (Table III) also has a strong continuous spectrum superimposed on the band system. It begins sharply at A2700 and disappears at 13300.

The *p*-xylene bands (Table IV) are quite strong and are easily visible against the continuous background which starts sharply at A2750 and extends to 13300.

TABLE III

TESLA LUMINESCENCE BANDS OF *m*-XYLENE

X in Å., Austin and Black	λ in Å., McVicker, Marsh and Stewart	ν in cm.$^{-1}$ ($\nu = 1/\lambda$) Austin and Black
	2673	
2703.6	2705	36977
2709.0		36903
2712.4	2712	36857
2721.4	2719	36735
2727.9	2730	36647
2735.0		36552
2742.6	2744	36451
	2750	
2758.0	2761	36247
2771.2	2765	36075
2784.0	2781	35909
2792.6		35798
2799.1	2802	35715
2813.7	2817	35530
2820.4		35446
2850.6		35070
2861.6		34935
2881.4		34695
2885.3		34648

TABLE IV

TESLA LUMINESCENCE BANDS OF *p*-XYLENE

X in Å., Austin and Black	λ in Å., McVicker, Marsh and Stewart	ν in cm.$^{-1}$ ($\nu = 1/\lambda$), Austin and Black
2704.3		36967
2709.3		36899
2715.4		36816
2721.3	2724	36736
2728.0		36646
2732.5	2732	36586
2736.1		36538
2742.5		36452
2745.0	2746	36419
2761.1		36207
2770.4		36085
2772.3	2774	36061
2784.7		35900
2786.1	2787	35882
2791.2		35816
2794.8	2794	35770
2799.8	2803	35706
2810.1	2812	35575
2814.5	2817	35520
2823.5	2824	35406
2830.0		35325
2850.5	2853	35071
2865.0	2869	34894
2881.2	2883	34698
2925.5	2922	34172
2951.3	2954	33874
2976.6		33586

The spectrum of ethylbenzene (Table V) has like all the rest a continuous background extending from a sharp lower limit at λ2667 to a very diffuse one at about λ3200; the bands are rather poorly defined.

TABLE V

TESLA LUMINESCENCE BANDS OF ETHYLBENZENE

λ in Å., Austin and Black	ν in cm.$^{-1}$ ($\nu = 1/\lambda$), Austin and Black	λ in Å., Austin and Black	λ in A.. McVicker, Marsh and Stewart	v in cm $^{-1}$ ($\nu = 1/\lambda$), Austin and Black
2660.9	37570	2711.9	2711	36864
2664.5	37519	2716.1		36807
2666.6	37490	2718.3	2725	36747
2670.0	37442	2733.0		36579
2672.0	37414		2740	
2676.7	37348	2752.2		36324
2681.1	37287	2777.5		35993
2689.3	37173	2802.4	2802	35673
2705.5	36951	2812.2	2817	35549
2709.4	36898			

Discussion

It became evident early in the work that an analytical method based on the equipment described would be quite unwieldy. The apparatus is costly and rather troublesome to assemble and the time required to make a good exposure, at least three hours, is rather long; moreover, the decomposition of the vapors makes it necessary to use a new discharge tube for each exposure. However, to gain some idea of the possible utility of the method one trial analytical run was made on the contents of a bottle marked "xylene" which had been standing around the laboratory for some time. On comparing the spectrogram of this unknown with those of the three pure xylenes it was found that the unknown contained all three isomers. The continuous background rendered the task of estimating the amount of each hopeless.

Thus far our attempts to apply the formulas of modern band spectroscopy to these data have not met with success. The problem is very difficult, much more so than in the case of benzene, because comprehensive data of the required accuracy are not available. Even were these at hand the complexity of the emitting molecule would make their interpretation far from simple However, it is interesting to consider our results in the light of some of the older and less precise generalizations. The first of these was set forth by Staudinger.[6] All chemical substitution which displaces the bands toward the red diminishes the state of saturation of the molecule. The second was made by Henri.[7] Organic bodies which react most easily, that is, are most labile, possess the strongest ultraviolet bands.

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[6] Staudinger, "Les Cetenes," Stuttgart, 1912, p 98

[7] Henri, *Compt.* rend., 156,1979 (1913).

Let us now apply the first law to our measurements. We may be sure that the extreme ultraviolet ends of the spectra are lacking because of the absorption by the unexcited vapor and therefore the terminations of the various spectra are not to be taken alone as criteria for displacement. We may, however, arrive at a more reliable standard for obtaining the shifts due to changes in composition by comparing certain sharp band heads which seem to correspond in each spectrum. On making such a comparison on our plates it appeared that the toluene bands are displaced to the red as compared to those of benzene. o-xylene showed an increased shift toward the red, while the *p*- and m-isomers were still further displaced. Ethylbenzene, however, gave a spectrum in the same general region as toluene

These shifts are confirmed by the spectra of these compounds in the solid at liquid-air temperatures[8] Under these conditions these band systems actually show terminal bands whose positions are easily compared. The shifts observed in these spectra are in agreement with the above results. The most significant difference is that the *p*-xylene is slightly, though definitely, shifted toward the red as compared to the m-compound.

Interpreted on the basis of Staudinger's law these shifts mean that benzene is the most saturated of the substances studied; toluene is less saturated; o-xylene is still less so, while the *p*- and m-isomers are the least saturated of all, which conclusions are borne out by the well-known chemical behavior of these compounds; this would indicate that the band spectra data are in complete accord with Staudinger's law.

When attention is directed to the law of Henri, an apparent difficulty arises at once, for the bands of benzene are easily the strongest and most complete, yet there can be no doubt as to the pronounced stability of benzene. This leads us to the conclusion that considerable care must be exercised in applying this "law" to organic compounds. One explanation of this apparent exception is that the intensity of the ultraviolet bands is dependent on the number of excited electrons, which, in general, is related to the relative ease of excitation. The chemical activity on the other hand depends on the ease with which electrons may be removed or shared, which is quite a different thing. Thus it may be possible to have an electronic structure capable of being easily excited by the proper radiation and yet resistant to actual change of configuration, *i. e.*, chemical reaction.

Another explanation of the unique character of the benzene bands may be sought in a study of the source of the emitted radiation. If it is assumed that each C and H atom can vibrate independently, there is at once an explanation of the greater intensity of the benzene bands.

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[8] Data shortly to appear in the *Bureau of Standards Journal of Research.*

Since each C and H atom is equal to all the others, it follows that the frequency of the light emitted will be independent of the portion of the ring from which it emanates and therefore the light in the frequencies which are emitted will be intense. This leads to a strong spectrum with sharp bands and little if any continuous background, which is just what benzene does give.

In the case of toluene a different state of affairs exists. One of the atoms is definitely marked by having a methyl group attached and the neighboring C atoms are probably slightly affected by the presence of this group; consequently, the various parts of the molecule when excited by the discharge do not all emit the same frequency but instead there appears a series of frequencies which are but slightly different. This leads to a group of strong bands arising from certain favored modes of vibration which are blurred by bands of slightly different frequency arising from other vibrations. An extension of this argument shows that it applies equally well to ethylbenzene and the xylenes. One would expect the bands of these substances to be less sharp than those of toluene, as indeed they are.

It should perhaps be emphasized here that these views are to be regarded as but tentative suggestions. The extreme complexity of the problem and the comparative lack of detail in the spectra of these simple derivatives render it difficult to be more specific in their interpretation.

A study of these spectra also leads one to believe that we should be more careful in keeping the meaning of our chemical symbols constantly in mind. All the existing theories of saturation and stability can be readily reconciled with the ordinary equilateral hexagonal formula for the simple benzene ring; indeed the observations force us to accept such a symbol. Whether the ring is coplanar or not is of small importance in this connection. On the other hand, it should be clearly recognized that the introduction of a group of any kind immediately sets up electrical and magnetic disturbances which are transmitted around the ring, and cannot fail to give a twist to the molecule so that to be accurate in our symbolism we should now write a warped or non-equiangular hexagon. The exact nature of this twist is not at present known but the accumulation of more data will undoubtedly elucidate this point. Meanwhile, we can keep in mind that the substituted benzene ring is not at all the same as the original symmetrical structure.

It is a pleasure to acknowledge our indebtedness to Professor H. S. Uhler for his advice in matters of spectroscopic technique, to Professor John Johnston for his general interest and help and to Mr. L. E. Faulhaber for help in preparing the manuscript. We wish also to thank the Commonwealth Fund for the fellowship held by one of us during the course of this research.

Summary

The emission spectra of toluene, ethylbenzene, *o*-, m- and *p*-xylene have been photographed using the Tesla discharge as a means of excitation; they are found to contain a number of bands generally accompanied by a continuous background. The numerical data are in agreement with previous measurements. A comparison of these spectra indicates that substitution produces a profound disturbance in the electrical and magnetic symmetry of the benzene ring. Further, these spectra have a limited application in qualitative analysis but are rendered less suitable for quantitative work because of the continuous background.

NEW HAVEN, CONNECTICUT

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

THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF LITHIUM NITRATE IN CERTAIN BINARY ALCOHOLIC SYSTEMS[1]

BY J. L. WHITMAN AND D. M. HURT

RECEIVED AUGUST 19, 1930 PUBLISHED DECEMBER 18, 1930

Investigations of conductivity in mixed solvents were first made by Lenz,[2] and have since been extended from time to time by many other workers. Perhaps the most systematic and extensive results have been obtained by Jones[3] and his co-workers using various solvents such as water, methyl alcohol, ethyl alcohol, propyl alcohol, acetone and glycerin, and a considerable number of solutes.

Data for the conductivity and viscosity of solutions of lithium nitrate in certain aqueous–alcoholic solvents have been reported in a previous paper.[4] As a continuation of these studies data are now given for systems containing various proportions of water, ethyl alcohol, n-propyl alcohol and isopropyl alcohol. In some cases density data have also been included.

Materials.—The lithium nitrate, water and ethyl alcohol were prepared and purified by the methods used by Whitman and Spencer. High grade n- and isopropyl alcohols from the Eastman Kodak Company were purified by the same method that was used in purifying ethyl alcohol. The specific conductivities of the purified solvents were as follows: water,

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[1] Prepared from a Dissertation presented to the Graduate Faculty of the State University of Iowa by D. M. Hurt, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Lenz, *Mem. l'acad. St. Petersburg*, *7*, *30* (1881); Stephan, *Wied. Ann.*, 17, 673 (1883); Arrhenius, *Z. physik. Chem.*, *9*, 487 (1892); Wakeman, *ibid.*, 11, 49 (1893); Zelinsky and Krapiwin, *ibid.*, **21,** 35 (1896); Cohen, *Wied.* ***Ann.*,** **25,** 31 (1898).

[3] For a summary and review of this work, see Jones and Kreider, *Am. Chem. J.*, 45, 282 (1911).

[4] Whitman and Spencer, THIS JOURNAL, 50,1840 (1928).

1.1×10^{-6}; ethyl alcohol, 0.85×10^{-6}; n-propyl alcohol, 4.96×10^{-6}; isopropyl alcohol, 0.51×10^{-6}.

Apparatus and Measurements.—A Leeds and Northrup slide wire bridge with extension coils, tunable head phones, Curtis coil resistance boxes, adjustable air condensers and the usual shieldings and sheathings were used. A Vreeland oscillator was used as the source of alternating current. Conductivity cells similar to those described by Schlesinger and Martin[5] were calibrated by the method of Kraus and Parker.[6] The cell constants were checked at frequent intervals during the course of the measurements.

Temperature measurements were made with a thermometer which had been compared with one certified by the Bureau of Standards. All measurements were made at 25 ± 0.01°. A well insulated, double-walled constant temperature bath of about 100 liters' capacity, filled with a light mineral oil, was used. Through a glass window in one side, readings were made on an Ostwald type quartz viscometer, which had a period for water of about eighteen minutes. Density determinations were made with a pycnometer of about 25 ml. capacity.

Conductivity data have been corrected for the conductivity of the pure solvent.

Experimental

Water-Ethyl Alcohol Mixtures (2).—The equivalent conductivities of solutions of lithium nitrate of various concentrations and in solvents ranging in composition from pure water to pure ethyl alcohol are recorded in Table I. This system has been previously studied by Jones and Lindsay,' but it was thought best to repeat the work since they obtained but three points on the curve. The conductivity data for the 0.1 molar and the 0.00625 molar solutions are shown graphically in Fig. 1. Absolute viscosities of water-ethyl alcohol mixtures according to Noack are also shown

TABLE I

THE EQUIVALENT CONDUCTIVITY OF LITHIUM NITRATE IN THE SYSTEM WATER–ETHYL ALCOHOL, AT 25°

Molar concn..	100% H_2O	90%	80%	70%	60%	50%	40%	30%	20%	10%	100% C_2H_5OH
0.1	90.56	71.61	56.25	44.39	37.68	33.49	30.39	27.90	25.44	22.51	17.47
.05	94.84	74.77	58.42	46.36	39.46	35.34	32.39	30.12	27.88	23.47	20.74
,025	98.87	77.45	60.34	48.27	40.91	36.92	34.15	32.09	30.26	28.28	24.07
,0125	102.14	79.33	62.03	49.16	41.86	37.95	33.59	32.08	31.75	29.83	27.36
,00625	105.45	81.25	63.21	49.37	43.42	39.14	34.39	32.68	33.41	32.38	30.40
Sp cond of pure solvent $\times 10^{-6}$	110	4.32	6.37	457	3.34	359	364	385	392	260	0.85

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[5] Schlesinger and Martin, THIS JOURNAL, 36, 1589 (1914).

[6] Kraus and Parker, *ibid.*, 44,2422 (1922).

[7] Jones and Lindsay. Am. *Chem. J.*, 28,329 (1902).

in Fig. 1.[8] The conductivity–composition curve is here shown in complete form and is more satisfactory than the curve given by Whitman and Spencer (Ref. 4, p. 1843) as constructed from the meager data of Jones and Lindsay.

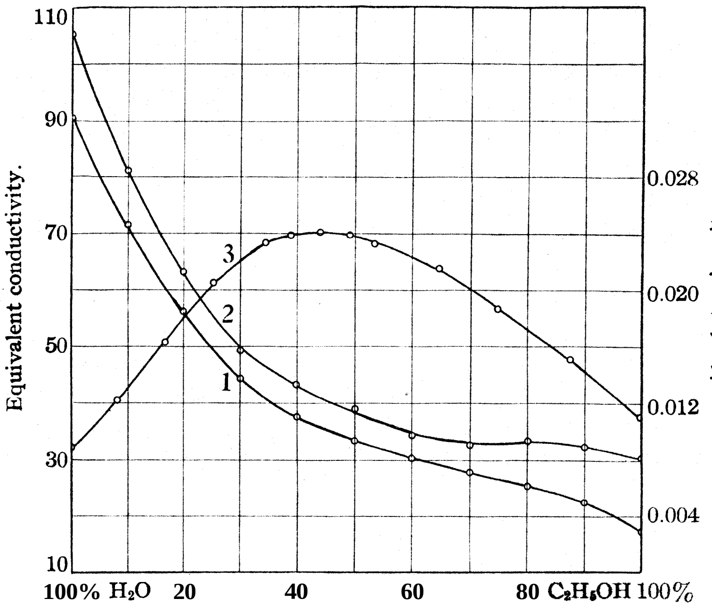

Fig. 1.—Lithium nitrate in water-ethyl alcohol mixtures. Curve 1, composition–conductivity, 0.1 M; Curve 2, 0.00625 M; Curve 3, composition–viscosity.

Water-n-Propyl Alcohol Mixtures (3).—Table II gives the equivalent conductivities for a series of solutions of lithium nitrate in various mixtures of water and n-propyl alcohol. Viscosities and densities of the various solvents are given in Table III, the values referring to water at 25°

TABLE II

THE EQUIVALENT CONDUCTIVITY OF LITHIUM NITRATE IN THE SYSTEM WATER–*n*-PROPYL ALCOHOL AT 25°

Molar concn.,	100% H_2O	90%	80%	70%	60%	50%	40%	30%	20%	10%	100% C_3H_7OH
0.1	90.56	69.92	53.96	45.14	38.15	31.99	26.33	21.10	16.41	11.85	5.564
.05	94.84	73.28	57.10	47.59	40.51	34.29	28.25	23.27	18.3.5	13.62	6.854
.025	98.87	76.93	59.53	49.93	42.64	36.72	30.49	25.37	20.25	15.94	8.381
.0125	102.14	80.50	61.53	51.73	44.17	39.05	32.63	27.28	22.00	18.13	10.10
.00625	105.45	84.63	64.26	53.18	45.66	41.23	34.44	28.80	25.07	20.72	11.86
Sp. cond of pure solvent $\times 10^{-6}$	1.1	11.7	20.3	28.6	32.7	30.1	31.8	27.9	23.5	14.2	4 9

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[8] John C Evans, "Physico-Chemical Tables," Griffin and Co., Ltd., London, 1911, p. 651.

TABLE III

VISCOSITIES AND DENSITIES OF WATER–*n*-PROPYL ALCOHOL MIXTURES AT 25°

H_2O, %	Viscosity	Density	H_2O, %	Viscosity	Density
100	0.008944	0.99704	40	0.02669	0.8964
90	.01233	.9853	30	.02644	.8742
80	.01668	.9730	20	.02490	.8515
70	.01944	.9626	10	.02232	.8269
60	.02362	.9372	0	.01962	.7957
50	.02575	.9170			

for which the values 0.008944 and 0.99704 were used. The corresponding curves are given in Fig. 2.

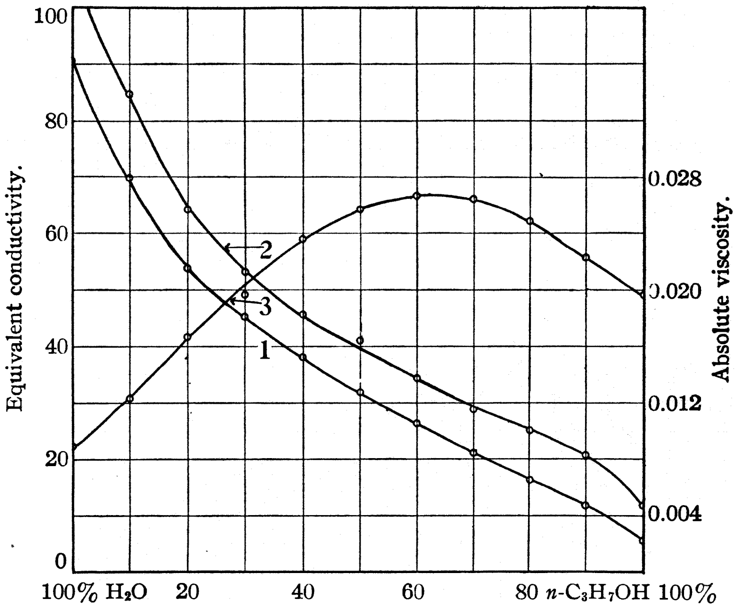

Fig. 2.—Lithium nitrate in water–*n*-propyl alcohol mixtures. Curve 1, composition-conductivity, 0.1 M; Curve 2, 0.00625 M; Curve 3, composition–viscosity.

Water–Isopropyl Alcohol Mixtures (4).—Table IV gives the conductivity data for solutions of lithium nitrate in water–isopropyl alcohol

TABLE IV

THE EQUIVALENT CONDUCTIVITY OF LITHIUM NITRATE IN THE SYSTEM WATER–ISOPROPYL ALCOHOL AT 25°

Molar concn.	100% H_2O	90%	80%	70%	60%	50%	40%	30%	20%	10%	100% C_3H_7OH
0.1	90.56	66.88	49.58	38.59	32.05	26.78	22.07	17.76	13.75	9.465	2.058
.05	94.84	70.39	52.36	40.76	33.77	28.56	24.01	19.53	15.54	11.07	2.447
.025	98.87	73.92	55.02	42.70	35.48	30.25	25.88	21.22	17.39	12.84	2.998
.0125	102.14	77.50	57.30	44.52	37.04	31.82	27.66	22.83	19.17	14.80	3.812
.00625	105.45	82.15	59.28	46.04	38.40	33.20	29.21	24.23	20.91	16.84	4.921
Sp. cond. of pure solvent $\times 10^{-6}$	1.1	2.86	1.92	1.56	1.24	1.03	1.46	1.80	2.86	0.90	0.51

TABLE V

VISCOSITIES AND DENSITIES OF WATER–ISOPROPYL ALCOHOL MIXTURES AT 25°

H_2O, %	Viscosity	Density	H_2O, %	Viscosity	Density
100	0.008944	0.99704	40	0.03139	0.8931
90	.01284	.9839	30	.03057	.8682
80	.01847	.9723	20	.02786	.8418
70	.02371	.9580	10	.02381	.8128
60	.02795	.9387	0	.02183	.7807
50	.03070	.9167			

mixtures; Table V, the viscosity and density data for the solvents. Curves are shown in Fig. 3.

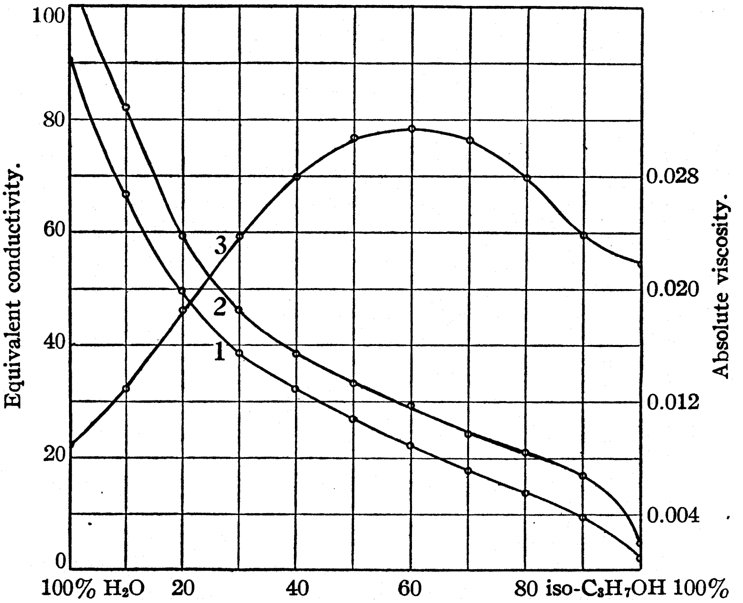

Fig. 3.—Lithium nitrate in water–isopropyl alcohol mixtures. Curve 1, composition-conductivity, 0.1 *M*; Curve 2, 0.00625*M*; Curve 3, composition–viscosity.

Ethyl Alcohol-n-Propyl Alcohol Mixtures (6).—Conductivity data are given in Table VI. Viscosity data are according to Herz,[9] the corresponding volume percentages having been calculated from his weight percentages by means of the necessary density data. Curves are given in Fig. 4.

Ethyl Alcohol-Isopropyl Mixtures (7).—Conductivity data are given in Table VII; viscosity and density data in Table VIII. Curves are shown in Fig. 5.

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[9] "Tables Ann. Internat. de Constantes," Vol. V, Gauthier-Villars et Cie., Paris, 1925, p. 54.

TABLE VI

THE EQUIVALENT CONDUCTIVITY OF LITHIUM NITRATE IN THE SYSTEM ETHYL ALCOHOL–*n*-PROPYL ALCOHOL AT 25'

Molar concn.	100% C_2H_5OH	90%	80%	70%	60%	50%	40%	30%	20%	10%	100% C_3H_7OH
0.1	17.47	15.66	14.04	12.86	11.73	10.50	9.427	8.375	7.370	6.455	5.564
.05	20.74	18.66	17.11	15.72	14.41	12.87	11.52	10.28	9.081	7.971	6.854
.025	24.07	22.14	20.26	18.80	17.27	15.42	13.94	12.41	11.02	9.724	8.381
.0125	27.36	25.62	23.46	21.86	20.22	18.10	16.48	14.68	13.23	11.66	10.10
.00625	30.40	28.31	26.30	24.78	22.99	20.71	18.96	16.84	15.38	13.58	11.85
Sp. cond. of pure solvent $\times 10^{-6}$	0.85	4.95	5.86	6.66	6.85	7.30	6.87	6.52	6.09	5.68	4.96

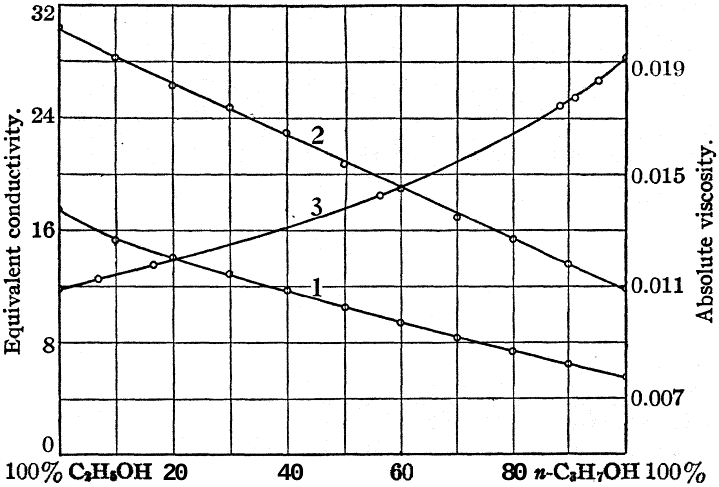

Fig. 4.—Lithium nitrate in ethyl alcohol–n-propyl alcohol mixtures. Curve 1, composition-conductivity, 0.1 *M*; Curve 2, 0.00625 *M*; Curve 3, composition–viscosity.

TABLE VII

THE EQUIVALENT CONDUCTIVITY OF LITHIUM NITRATE IN THE SYSTEM ETHYL ALCOHOL–ISOPROPYL ALCOHOL AT 25°

Molar concn.	100% C_2H_5OH	90%	80%	70%	60%	50%	40%	30%	20%	10%	100% C_3H_7OH
0.1	17.47	14.88	12.99	11.30	9.741	8.282	6.854	5.498	4.179	3.071	2.058
.05	20.74	17.42	15.99	13.92	12.01	10.22	8.513	6.853	5.233	3.981	2.447
.025	24.07	21.31	18.24	16.80	14.59	12.47	10.50	8.478	6.573	5.078	2.998
.0125	27.36	24.25	22.05	19.92	17.35	14.98	12.66	10.48	8.264	6.478	3.812
.00625	30.40	27.80	25.36	22.94	20.19	17.66	15.21	12.84	10.31	8.222	4.921
Sp. cond. of pure solvent $\times 10^{-6}$	0.85	2.56	2.60	2.54	2.04	1.57	1.23	0.88	0.60	0.46	0.51

n-Propyl Alcohol–Isopropyl Alcohol Mixtures (a).—Conductivity data are given in Table IX; viscosity and density data, in Table X. Curves are shown in Fig. 6. Fewer mixtures were used in this system since it was expected that a very nearly linear relationship would be found. Results show this to be true.

TABLE VIII

VISCOSITIES AND DENSITIES OF ETHYL ALCOHOL–ISOPROPYL ALCOHOL MIXTURES AT 25°

C_2H_5OH, %	Viscosity	Density	C_2H_5OH, %	Viscosity	Density
100	0.01095	0.7852	40	0.01605	0.7827
90	.01150	.7849	30	.01709	.7823
80	.01224	.7843	20	.01856	.7819
70	.01302	.7839	10	.01985	.7822
60	.01388	.7835	0	.02183	.7807
50	.01485	.7832			

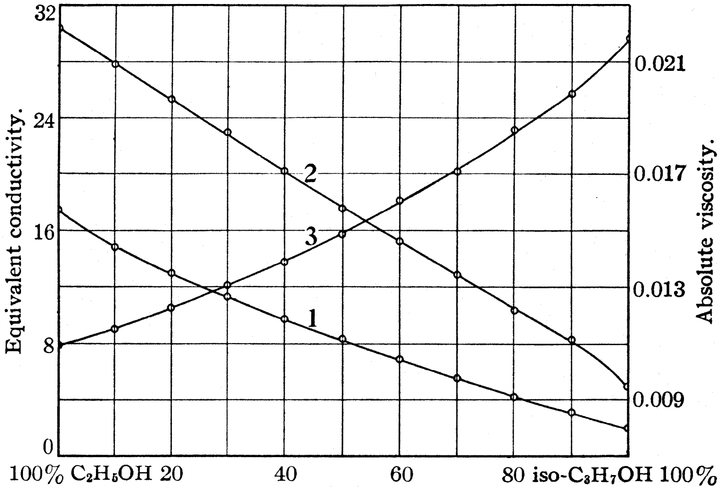

Fig. 5.—Lithium nitrate in ethyl alcohol–isopropyl alcohol mixtures. Curve 1, composition-conductivity, 0.1 M; Curve 2, 0.00625 *M*; Curve 3, composition–viscosity.

TABLE IX

THE EQUIVALENT CONDUCTIVITY OF LITHIUM NITRATE IN THE SYSTEM *n*-PROPYL ALCOHOL–ISOPROPYL ALCOHOL AT 25°

Molar concn.	100% *n*-C_3H_7OH	80%	60%	40%	20%	100% iso-C_3H_7OH
0.1	5.564	4.886	4.174	3.452	2.782	2.058
.05	6.854	6.023	5.133	4.267	3.419	2.447
.025	8.381	7.389	6.349	5.325	4.276	2.998
.0125	10.10	8.998	7.853	6.664	5.349	3.812
.00625	11.85	10.76	9.518	8.272	6.792	4.921
Sp. cond. of pure solvent × 10^{-6}	4.96	4.12	3.16	2.29	1.39	0.51

TABLE X

VISCOSITIES AND DENSITIES OF *n*-PROPYL ALCOHOL–ISOPROPYL ALCOHOL MIXTURES AT 25°

n-C_3H_7OH, %	Viscosity	Density	*n*-C_3H_7OH, %	Viscosity	Density
100	0.01962	0.7957	40	0.02082	0.7889
80	.02004	.7962	20	.02130	.7852
60	.02040	.7924	0	.02183	.7807

Discussion

The various systems studied have been numbered and will subsequently be referred to by number. Nos. 1 and 5 are the water–methyl alcohol and methyl alcohol–ethyl alcohol systems, respectively, previously reported by Whitman and Spencer.

In systems 1, 2, 3 and 4, *i. e.*, those which contain water as one of the components of the solvent, a maximum viscosity is found for some composition. In only one of these, No. 1, does the conductivity-composition curve exhibit a minimum. In systems 5, 6, 7 and 8, *i. e.*, those systems which contain two alcohols as the components of the solvent, no maxima or minima are observed in either the viscosity or the conductivity curves.

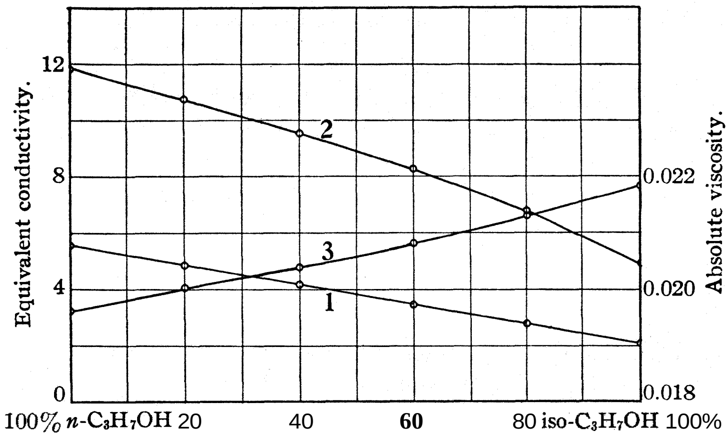

Fig. 6.—Lithium nitrate in n-propyl–isopropyl alcohol mixtures. Curve 1, composition–conductivity, 0.1 M; Curve 2, 0.00625 M; Curve 3, composition–viscosity.

In several of the latter cases the curves are very nearly straight lines, as might be expected since the components of the solvent are very similar chemically.

Jones concluded that a minimum in the conductivity curve was the direct result of the increase in viscosity. However, in attempting to explain this minimum other factors must also be considered, such as change in degree of dissociation with change in composition of solvent. But Jones[10] found that the degree of dissociation in a solvent containing 50% water and 50% methyl alcohol was greater than that in either pure solvent. This factor should therefore cause an increase in conductivity. It is thus evident that the viscosity explanation alone is far from satisfactory as a means of explaining the observed conductivity changes.

The viscosity data here recorded are believed to be accurate to ap-

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[10] Jones and Carroll, *Am. Chem. J.*, 32, 521 (1904)

proximately 0.05%. For the viscometer used the time of outflow for water was approximately 1000 sec., while the stop-watch used was accurate to 0.2 sec. An error of 0.4 sec. in time would thus introduce an error of 0.04%. If the weighings involved were accurate to only 1 mg., then the errors of weighing for the pycnometer used (about 25 g. capacity) would amount to only 0.004%. According to the "International Critical Tables," Vol. V, p. 10, the change in viscosity of water per 0.01' at 25° is approximately 0.02%. Thus the appreciable errors will total not more than 0.06% and it is believed that an error of 0.05% represents the reasonable degree of precision of results obtained.

It should be noted that the values recorded for the water–*n*-propyl alcohol system are probably the least accurate of the conductance data, since the solvent corrections for this system are unusually large.

Summary

1. Measurements have been made of the conductivities of lithium nitrate in the mixed solvents containing various proportions of the following components: water, ethyl alcohol, *n*-propyl alcohol and isopropyl alcohol.

2. Viscosity and density determinations have also been made on the same pure solvent systems.

TEXAS CHRISTIAN UNIVERSITY
FORT WORTH, TEXAS

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 269]

THE EFFECT OF LIGHT ON THE FERROCYANIDE–FERRICYANIDE IODINE–IODIDE EQUILIBRIUM

BY ROSCOE G. DICKINSON AND S. FREDERICK RAVITZ

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It is well known that ferric salts oxidize iodides in aqueous solution at a moderate rate and that ultimately an equilibrium, $2Fe^{+++} + 2I^{-} \rightleftharpoons 2Fe^{++} + I_2$, is reached. Sasaki[1] investigated the effect of light on systems containing the substances involved in this equilibrium. Using sunlight and light from an incandescent lamp, he found that the illuminated systems always contained less titratable iodine than similar unilluminated systems. He further adduced evidence that the effect of the light was a displacement of the equilibrium rather than some other mode of disappearance of iodine. Further photochemical experiments were made by Rideal and Williams[2] who concluded, among other things, that the region of visible photoactive radiation was within the range 5500-6500 Å., and that one quantum of absorbed radiant energy caused one molecule of iodine to react. However,

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[1] N. Sasaki, *Z. anorg. Chem.*, **122**, 61 (1922).

[2] E. K. Rideal and E. G. Williams, *J. Chem. Soc.*, **127**, 258 (1925).

Kistiakowsky[3] extended these experiments and concluded that radiations of the wave lengths 5460, 4360 and 3660 Å. were all effective; determinations of the quantum yield showed a disappearance of approximately one molecule of iodine per quantum absorbed at each of these three wave lengths.

In systems containing the ions $Fe(CN)_6^{\equiv}$ and $Fe(CN)_6^{==}$ instead of the ions Fe^{+++} and Fe^{++}, the thermal rates of reaction are again moderate, and directly measurable equilibria are again attained. The reaction may be expressed by the equation $2Fe(CN)_6^{\equiv} + 2I^- \quad 2Fe(CN)_6^{==} + I_2$. Both the kinetics and the equilibria in these systems have been the subject of considerable study.[4] We have found that such systems are sensitive to light not absorbed by the complex cyanides. However, preliminary experiments showed that when light was directed into an equilibrium mixture containing the complex cyanides, free iodine was produced rather than consumed. The present paper describes experiments in which the light sensitivity of solutions containing the complex ions is compared with that of solutions containing the simple ions.

Apparatus

The source of illumination was a 500-watt lamp whose filament covered an area about 1.3 cm. square. The lamp was controlled with the aid of a variable resistance and an ammeter in series with it; the lamp current was maintained constant at 4.3 amperes. Light from this lamp passed through a 6% copper sulfate solution in a flat cell, 1 cm. thick; this filter absorbed the infra-red. This cell was fastened to the front of the thermostat, which was a large flat-sided glass jar, so as to leave a pocket 3 cm. in thickness between the cell and the jar. In this pocket was placed a second filter mounted on a sheet of brass with a rectangular opening; this filter served to isolate the desired spectral region. The pocket was filled with water to minimize reflection losses. The reaction cell which contained the solution to be illuminated was a flat-sided bottle, the face of which was 4.5 × 10 cm., and the thickness 2.86 cm. This reaction cell was silvered externally except on the face toward the lamp. The thermostat with its attached filters was contained in a box provided with a shutter and thermal insulation. Arrangement was made so that the lamp and cell could, from one experiment to another, be brought into the same positions. The experiments were carried out at 0°; to permit this, the thermostat was kept well packed with clean ice except in front of the reaction cell, which was close to the thermostat wall. Water was circulated from bottom to top of the thermostat by an air lift. Ice was also kept in the upper part of the filter pocket.

Analytical Method

The solutions to be analyzed, whether ferrous–ferric iodine–iodide mixtures or ferrocyanide–ferricyanide iodine–iodide mixtures, were ordinarily not greatly removed

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[3] G. B. Kistiakowsky, THIS JOURNAL. 49, 976 (1927).

[4] F. G. Donnan and R. Le Rossignol, *J. Chem. Soc.*, 83, 703 (1903); G. Just, *Z. physik. Chem.*, 63,513 (1908); C. Wagner, *ibid.*, 113,261 (1924); V. K. La Mer and K. Sandved, THIS JOURNAL, 50, 2656 (1928); V. K. La Mer and H. B. Friedman, *ibid.*, 52, 876 (1930).

from equilibrium. They were analyzed for free iodine by the following method: from a 0.1 *N* thiosulfate solution, a solution of convenient strength, usually 0.004 *N*, was freshly prepared by dilution. Five cc. of this solution was pipetted into 50 cc. of water and starch was added. A sample of the solution to be analyzed was withdrawn from the reaction cell into a 10-cc. graduated pipet. The solution was then immediately run from this pipet into the thiosulfate solution to the appearance of a blue color, permanent on stirring. The elapsed time between the withdrawal of the sample and the attainment of the end-point was less than two minutes, and most of the solution analyzed was discharged into the thiosulfate in considerably less time. The suitability of this method for the titration of solutions containing ferrocyanide and ferricyanide has been discussed by La Mer and Friedman and by La Mer and Sandved.[5]

The Nature of the Photochemical Reaction

As mentioned above, when light is directed into a ferrocyanide–ferricyanide iodide–iodide equilibrium mixture, the concentration of titratable iodine increases. We have supposed that this increase in iodine concentration arises from a displacement of the equilibrium, *i. e.*, from the oxidation of iodide by ferricyanide. If this be the case then a solution which has been removed from equilibrium by shining in light should, when placed in the dark, return to equilibrium at the same rate as a solution of the same composition which has been equally removed from equilibrium by some other method, for example, by the dilution of a more concentrated equilibrium solution. We have tested this by the following experiment, which was carried out in an atmosphere of nitrogen in order to eliminate possible oxidation by dissolved air.

Tank nitrogen which had been bubbled through two bottles of strong alkaline pyrogallol solution and one bottle of water was used. All flasks used were first filled with nitrogen by filling them with water and displacing the water with nitrogen. Solutions were made up of distilled water which had been boiled for several minutes and allowed to cool with a fairly strong stream of nitrogen passing through it; the solutions were transferred from one flask to another by the use of nitrogen pressure.

Sixteen grams of c. p. potassium ferricyanide was dissolved in about 100 cc. of water, filtered into a 500-cc. volumetric flask, and a vigorous stream of nitrogen was passed through the solution for several minutes; 20.00 g. of c. p. potassium iodide was likewise dissolved in about 100 cc. of water and nitrogen was passed through this solution for several minutes. It was then transferred to the volumetric flask and water was added to the 500-cc. mark. The resulting mixture was transferred to an Erlenmeyer flask and nitrogen was passed through it for about ten minutes, during which time very little iodine was formed. The mixture was then carefully packed with ice and allowed to stand for several days at 0° until equilibrium was practically attained.

To 250 cc. of the resulting equilibrium solution at 0° an equal volume of oxygen-free water (previously cooled to 0°) was added. The flask containing the resulting solution was packed in ice water and allowed to stand in the dark. Samples of this diluted solution were withdrawn at intervals by forcing the solution into the 10-cc. graduated pipet with nitrogen pressure, and were titrated by the method described above. The results of these titrations are plotted as circles in Fig. 1.

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[5] V. K. La Mer and H. B. Friedman, This Journal, 52, 877 (1930); V. K. La Mer and K. Sandved, *ibid.*, 50, 2659 (1928).

After about twenty-four hours, this diluted solution had nearly reached equilibrium; 160 cc. of it was then transferred to the reaction vessel in the ice thermostat and illuminated for three hours through the copper sulfate filter and a 1-cm. layer of 16% potassium chromate solution. Immediately upon ceasing the illumination the solution was placed in the dark and samples were withdrawn at intervals and titrated as before.

The results of this series of titrations are shown as crosses in Fig. 1; the time origin for the plot relating to the illuminated solution was so chosen that the first point (highest iodine concentration) fell on the curve relating to the unilluminated solution. If the effect of light was simply the displacement of equilibrium, then the concentrations of all materials should be the same in the two solutions at this point. It may be seen from Fig. 1 that these two solutions returned toward equilibrium at the same rate at all times. Moreover, the final iodine concentration arrived at was the same in each case; twenty-nine hours after the beginning of each experiment that for the illuminated solution had become 0.00396 and that for the unilluminated solution, 0.00398 N.

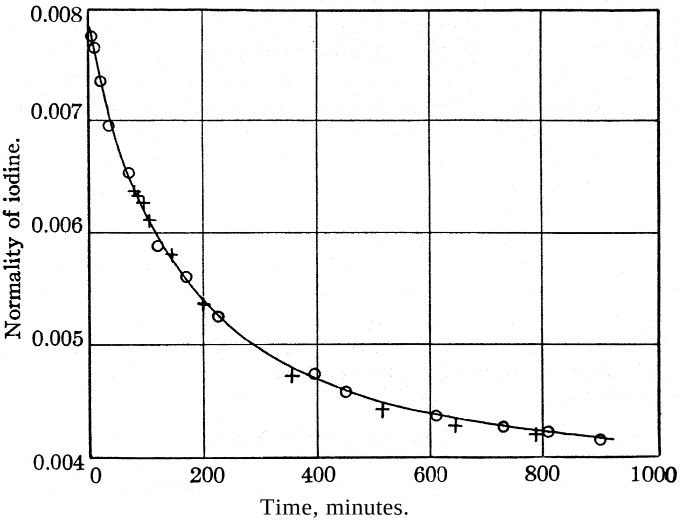

Fig. 1.—Comparison of change of iodine concentration with the time for two solutions of the same composition, one (circles) having been removed from equilibrium by dilution, the other (crosses) having been illuminated. The curve is drawn through the circles.

When similar experiments were carried out without the precaution of excluding air, the coincidence of the two curves was not so complete and was especially incomplete if the illumination was a prolonged one; a solution which had been given twenty hours' illumination finally came in the dark to an equilibrium concentration of iodine about 12% lower than that of a corresponding unilluminated solution.

In the experiments of Fig. 1, the concentration of the iodine before illumination was 0.00398 N; the equivalent concentration of the ferrocyanide (since the solution was made up from ferricyanide and iodide) was the same. During illumination, the iodine concentration rose to 0.00636 N, an increase of 60%. If this increase were not due to a shift in the equilibrium, the illuminated solution would then not be expected to contain the same amount of ferrocyanide as the unilluminated solution of equal iodine concentration prepared by dilution, and an equality in the rate of return to equilibrium would not be expected, nor should the same equilibrium concentration of iodine be reached in the two cases. We take the observed equality as evidence that the photochemical reaction with the radiation used is a reduction of ferricyanide to ferrocyanide by iodide.

Further evidence that this is the case is furnished by the following experiment in which the formation of ferrocyanide on illumination is shown directly. Two solutions, the first 0.008 N in iodine and 0.016 formal in potassium iodide, and the other 0.010 M in potassium ferricyanide, were made up with no effort to exclude air, and brought to 0°. Equal volumes of the two solutions were then mixed, and half the resulting solution was immediately transferred to a reaction vessel placed in the ice thermostat. Illumination with the 500-watt lamp (through the copper sulfate and potassium chromate filters as above) was started at once. At intervals 10-cc. samples of the illuminated and of the unilluminated solutions were withdrawn simultaneously and pipetted into large test-tubes, each containing 50 cc. of water at 0° to which had been added 2 cc. of a 2% solution of ferric ammonium sulfate in 0.012 N sulfuric acid. After five minutes' illumination the test with the illuminated solution gave a decided blue color of ferric ferrocyanide, whereas the test with the unilluminated solution showed no visible trace of blue. After ten minutes the results were similar, the color obtained with the illuminated solution being somewhat stronger than before. After twenty minutes the illuminated solution gave a still stronger color, while the unilluminated solution now gave a faint blue color resulting from the formation of ferrocyanide in the comparatively slow thermal reaction.

The Quantum Yield

A series of experiments was made in which the photochemical rate of production of iodine in ferrocyanide–ferricyanide mixtures was compared with the rate of disappearance of iodine in ferrous–ferric mixtures. In carrying this out, a pair of solutions, one of each kind, was made up and the solutions allowed to come substantially to equilibrium at 0°; the concentrations were so chosen that the titratable iodine content was about the same in each. The ferrocyanide–ferricyanide solutions were all made up as described in the previous section, by starting with 16.00 g. of potassium ferricyanide and 20.00 g. of potassium iodide; in different experiments, the extent of dilution was varied. The ferrous–ferric solutions were made up by dissolving 4.82 g. of ferrous ammonium sulfate and 0.66 g. of ammonium sulfate in water containing 4.2 cc. of 6 N sulfuric acid; to this was added a solution of 3.74 g. of potassium iodide and the resulting solution diluted so as to give the desired free iodine concentration. The solutions were successively exposed in the same reaction cell under the same conditions. During each exposure samples with withdrawn from time to time and titrated.

The results of two typical pairs of such experiments are shown plotted in Fig. 2. The abscissas are the time of exposure in minutes and the ordinates are the concentration of titratable iodine in millimoles per liter. Only at the beginning of each exposure can the rate of change of iodine concentration be considered to be due to light alone; when sufficient departure from thermal equilibrium has been attained, the thermal reverse reaction should lower the rate of change of iodine concentration. We have sought to decrease this difficulty by working at 0°. With exposures of one hour, in our apparatus, no appreciable change in rate was observable; consequently, as in Fig. 2, a straight line has been taken as the best representation of the data.

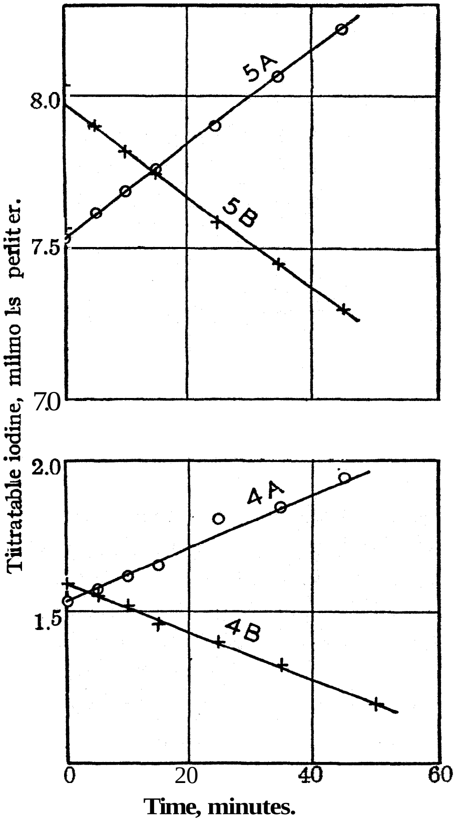

Fig. 2.—Change of iodine concentration with the time in ferrocyanide–ferricyanide solutions (circles) and in ferrous-ferric solutions (crosses) under the same illumination.

The results of all pairs of experiments are summarized in Table I. The concentrations, given throughout in millimoles per liter, apply to the beginning of exposure. In Col. 2 is given the concentration of titratable iodine; this is equal (since the solutions were made up from iodide and ferricyanide or ferric iron) to one-half the millimolal concentration of ferrocyanide or ferrous iron as the case may be. The total iodide, given in Col. 3, is the iodide taken minus the milliequivalents of titratable iodine. The concentrations of ferricyanide or ferric iron in Cols. 4 and 5 are similarly obtained from the titratable iodine and the amounts of ferricyanide or ferric iron taken. In Col. 6 is given the fraction of the titratable iodine existing as I_3^-. This was obtained using the equilibrium constant $(I^-) \times (I_2)/(I_3^-) = 0.000686$, which is the value obtained by Jones and Hartmann[6] in 0.1 *N* potassium iodide. Although the solutions involved here are by no means perfect, the calculations suffice to show that most of the titratable iodine was in the form of I_3^-.

The potassium chromate filter used in addition to the copper sulfate

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[6] G. Jones and M. L. Hartmann, This Journal, 37, 241 (1915).

TABLE I

RELATIVE RATES OF PRODUCTION OF IODINE IN FERROUS–FERRIC AND IN FERROCYANIDE–FERRICYANIDE SOLUTIONS

	Concentrations in millimoles per liter					Rate of production of titratable iodine, millimoles/liter-min.	
No.	Titratable iodine = $^1/_2(Fe(CN)_6^{\equiv\equiv})$ or $^1/_2(Fe^{++})$	Total iodide	$(Fe(CN)_6^{\equiv})$	(Fe^{+++})	$\frac{(I_3^-)}{(I_2) + (I_3^-)}$		Ratio of rates
1a[a]	1.71	117.2	45.3	..	0.995	+0.0108	1.03
1b[a]	1.71	7.10	..	1.25	.889	− .0105	
2a[a]	1.87	116.8	44.9	..	.995	+ .0111	1.03
2b[a]	1.78	7.64	..	1.51	.899	− .0108	
3a	1.34	87.6	33.7	..	.993	+ .0085	1.08
3b	1.46	8.52	..	2.26	.912	− .0079	
4a	1.53	98.9	38.1	..	.994	+ .0086	1.07
4b	1.59	8.25	..	1.99	.906	− .0080	
5a	7.53	225.9	82.2	..	.997	+ .0152	1.00
5b	7.98	29.04	..	4.04	.969	− .0151	
6a	7.59	225.8	82.1	..	.997	+ .0152	1.07
6b	7.93	29.13	..	4.13	.968	− .0142	
7a[a]	1.86	116.9	45.0	..	.995	+ .0008	0.16
7b[a]	1.96	5.58	..	1.08	.893	− .0050	

[a] Air was not excluded. Filters: K_2CrO_4 and $CuSO_4$ in Expts. 1-6 inclusive; methyl violet, $Cu(NO_3)_2$ and $CuSO_4$ in Expt. 7.

filter in Expts. 1–6 inclusive was a 1-cm. layer of 16% solution. Examination with a spectroscope showed that this filter removed substantially all radiation below 5000 Å. None of the materials involved in the experiments except I_3^- and I_2 gives appreciable absorption of visual radiation of wave lengths longer than 5000 Å. when present in the amounts used. Consequently all of the light absorption is attributed to I_3^- and I_2. The total light absorption in any ferrocyanide–ferricyanide solution must have been nearly the same as in the companion ferrous–ferric solution, for the proportion of titratable iodine in the form I_2 was not large even in these latter cases. Moreover, unpublished measurements made by Mr. C. F. Carlson in this Laboratory have shown that the absorption coefficient of I_2 is the same as that of I_3^- at about 5500 Å., and that the absorption coefficients do not change rapidly in this neighborhood.

In Col. 8 of Table I are given the ratios of the rates of appearance of iodine in the ferricyanide solutions to the rates of disappearance in the companion ferric solutions. For Expts. 1–6 inclusive, where the light absorption was due simply to I_3^- (and I_2), the ratios are within a few per cent. of unity in all cases, *i. e.*, the quantum yield of the two reactions is substantially the same. If we may assume that the quantum yield in the ferrous–ferric solutions is the same at 0° as in Kistiakowsky's quantum yield determinations, we are led to conclude that in the ferricyanide reaction, one molecule of iodine is formed per quantum absorbed by I_3^-.

Experiment 7 was made using filters of methyl violet and copper nitrate solutions; the combination absorbed strongly above 5000 Å. and transmitted freely below 4700 Å. It accordingly transmitted radiation which was absorbable by ferricyanide as well as by I_3^-. In this case the rate in the ferricyanide solution fell considerably below that in the ferric solution. Apparently, then, absorption by ferricyanide leads to little, if any, production of iodine.

Discussion

In the present photochemical experiments resulting in the reduction of ferricyanide, the absorbing species was almost exclusively I_3^-. The formation of a theory of this reaction is hampered by lack of knowledge of the elementary act accompanying the light absorption. In reviewing the photochemical ferrous-ion oxidation, Kistiakowsky[7] considered two reaction mechanisms to be possible

$$\begin{array}{ll} \text{(I)} & I_3^- + h\nu \longrightarrow I^- + 2I \\ & I + Fe^{++} \longrightarrow I^- + Fe^{+++} \\ \text{(II)} & I_3^- + h\nu \longrightarrow I_3^- \text{ (activated)} \\ & I_3^- \text{ (activated)} + Fe^{++} \longrightarrow 2I^- + Fe^{+++} + I \\ & I + Fe^{++} \longrightarrow Fe^{+++} + I^- \end{array}$$

Neither elementary act here provides very naturally for the reduction of $2Fe(CN)_6^{\equiv}$, but either can be made to do so by supplementing with the reaction $I + I^- \longrightarrow I_2^-$ and supposing that I_2^- (as well as I_3^- (activated) in II) can act as a reducing agent. The hypothetical ion I_2^- has been employed by Wagner[8] to account for the inhibiting effect of the products in the thermal reactions

$$2Fe^{+++} + 2I^- \longrightarrow 2Fe^{++} + I_2 \quad \text{and}$$
$$2Fe(CN)_6^{\equiv} + 2I^- \longrightarrow 2Fe(CN)_6^{\equiv -} + I_2$$

and for this purpose has been attributed both oxidizing and reducing properties. If it be introduced here, the following mechanisms of ferricyanide reduction result

$$\begin{array}{ll} \text{(I)} & I_3^- + h\nu \longrightarrow I^- + 2I \\ & I + I^- \longrightarrow I_2^- \\ & I_2^- + Fe(CN)_6^{\equiv} \longrightarrow I_2 + Fe(CN)_6^{\equiv -} \\ \text{(II)} & I_3^- + h\nu \longrightarrow I_3^- \text{ (activated)} \\ & I_3^- \text{ (activated)} + Fe(CN)_6^{\equiv} \longrightarrow I_2 + I + Fe(CN)_6^{\equiv -} \\ & I + I^- \longrightarrow I_2^- \\ & I_2^- + Fe(CN)_6^{\equiv} \longrightarrow I_2 + Fe(CN)_6^{\equiv -} \end{array}$$

To these may be added a mechanism based on a third elementary act

$$\begin{array}{ll} \text{(III)} & I_3^- + h\nu \longrightarrow I_2^- + I \\ & I + I^- \longrightarrow I_2^- \\ & I_2^- + Fe(CN)_6^{\equiv} \longrightarrow I_2 + Fe(CN)_6^{\equiv -} \end{array}$$

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[7] G. B. Kistiakowsky, "Photochemical Processes," Chemical Catalog Co., Inc., New York, 1928, p. 65.

[8] C. Wagner, *Z. physik.* Chem., 113, 261 (1924).

Any of these mechanisms is readily reconciled with our present knowledge of the photochemical ferrous-ion oxidation.

In an investigation of the photochemical reaction between potassium oxalate and iodine in iodide solution, Berthoud and Bellenot[9] developed a mechanism of that reaction which led to their empirical kinetic expression; this mechanism supposed that light absorbed by I_2 (producing iodine atoms) was effective while light absorbed by I_3^- was ineffective. This mechanism would then rule out any elementary act in which iodine atoms are produced from I_3^-; this would eliminate I and III above. However, we are at present disinclined to accept this conclusion; for it is possible to set up a mechanism leading to the kinetic expression of Berthoud and Bellenot without assuming light absorbed by I_3^- to be ineffective.[10]

In conclusion we may say that whatever the elementary act accompanying light absorption by I_3^- may be, it is clear that in it or in the subsequent reactions both oxidizing and reducing configurations are produced which are not to a great extent present in the unilluminated solution. The tentative assumption of the ion I_2^- is a simple hypothesis which satisfies these requirements.

Summary

It is found that when a ferrocyanide–ferricyanide iodine–iodide solution is illuminated with light absorbable by I_3^- but not by the complex cyanides, reduction of ferricyanide and oxidation of iodide occurs. The quantum yield is found to be substantially the same as that in the oxidation of ferrous ion in iodine–iodide solutions. Some possible mechanisms of the reaction are discussed.

PASADENA, CALIFORNIA

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[9] A. Berthoud and H. Bellenot, J. *chim. phys.*, *21*, *308* (1924); *Helv. Chim. Acta*, 7, 307 (1924).

[10] This is accomplished, for example, by the following mechanism which is similar to that of Berthoud and Bellenot but differs from it in two important respects: (1) light absorbed by I_3^- is effective; (2) the inhibiting effect of I^- is attained through the formation of I_2^- from I^- and I. The reactions are:

$$\begin{array}{llll} & h\nu + I_3^- & \longrightarrow I_2^- + I \text{ (or } I^- + 21) & (1) \\ & I + C_2O_4^{=} & \longrightarrow C_2O_4^- + I^- & (2) \\ & I_3^- + C_2O_4^- & \longrightarrow 2CO_2 + I_2^- + I^- & (3) \\ \text{or} & I_2 + C_2O_4^- & -\!\!+\ 2CO_2 + I_2^- & \\ & I_2^- + I_2^- & \longrightarrow I_3^- + I- & (4) \\ & I + I^- & \rightleftharpoons I_2^- & (5) \end{array}$$

If the equilibrium (5) is assumed to be rapidly established, the usual treatment leads to the expression

$$-\frac{d(C_2O_4^{=})}{dt} = k_2K_5\sqrt{\frac{k_1}{k_4}I_0\,(I_3^-)}\ (\text{Cod-})$$

for the case of low absorption, which agrees with that of Berthoud and Bellenot.

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

KINETICS OF THE REACTION BETWEEN PERSULFATE AND THIOSULFATE IONS IN DILUTE AQUEOUS SOLUTION

BY CECIL V. KING AND OTTO F. STEINBACH

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In the year 1897 Marshall[1] found that if a very slight stoichiometric excess of potassium persulfate were allowed to react with potassium thiosulfate, he could prepare pure tetrathionate. He also found that if excess thiosulfate were used, he could prepare trithionates.[2] These experiments are reviewed by Price,[3] who, however, did not investigate the reactions himself.

Marshall used rather concentrated solutions and did not study the speed of the reaction. No such study has been made until the present time, although the reaction was investigated from a quantitative standpoint by Schwicker.[4]

Schwicker found that in dilute solution in the cold the reaction was very slow, but that if a small amount of persulfate were boiled with excess $N/10$ thiosulfate, titration with iodine showed quantitative oxidation to tetrathionate. With potassium iodide present the oxidation to tetrathionate was also quantitative and much faster.

Experiments in this Laboratory[5] confirmed the fact that in dilute solution, at room temperature, the formation of tetrathionate is quantitative, within a few tenths of one per cent. with either persulfate or thiosulfate in considerable excess, with or without potassium iodide present.

A series of preliminary experiments on the velocity of the reaction in dilute solution[6] showed some interesting results. First, the reaction is catalyzed enormously by copper salts, much less by iron salts, very little by silver salts; other catalysts are quinone, quinhydrone and hydroquinone. Second, impurities in the water or the salts used have a large and uncontrollable catalytic effect. Consequently, most of the experiments reported here were carried out with water redistilled from dilute permanganate. Third, although the uncatalyzed reaction is stoichiometrically trimolecular

$$S_2O_8^{=} + 2S_2O_3^{=} \longrightarrow 2SO_4^{=} + S_4O_6^{=}$$

kinetically it follows the unimolecular law with some tendency in certain solutions to deviate in the direction of a zero or second order reaction.

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[1] Marshall, J. *Soc. Chem. Ind.*, 16, 396 (1897).

[2] Mackenzie and Marshall, J. *Chem. Soc.*, 93, 1726 (1908).

[3] Price, "Peracids and Their Salts," Longmans. 1912, p. 36.

[4] Schwicker, *Z. anal. Chem.*, 74, 433 (1928).

[5] By Miss Elinor Cook.

[6] Most of the experiments by Mr. Abraham Berkowitz.

Over a considerable range of concentrations, in ordinary distilled water or specially purified water, the velocity is unimolecular with respect to the persulfate ion and almost, though not quite, independent of the thiosulfate concentration.

Materials and Methods

Potassium persulfate was recrystallized from ordinary distilled or redistilled water between 50 and 0° until free from sulfate and dried over sulfuric acid. Standard solutions were made by direct weighing. Sodium thiosulfate was recrystallized two or three times, dried in air and the solutions made up in freshly boiled water; 0.08 M solutions in ordinary distilled or redistilled water were standardized by the persulfate–iodide or the permanganate method, and did not change their titer over periods as long as four months.

Potassium iodide, chloride and sulfate were recrystallized similarly, dried in air at suitable temperatures and standard solutions made by direct weighing of the salts. A stock solution of copper sulfate was made from recrystallized $CuSO_4 \cdot 5H_2O$ and standardized by adding potassium iodide and titrating the liberated iodine, as recommended by Fales.[7] The solutions used were made from this by quantitative dilution.

In the preliminary experiments mentioned before, the persulfate and thiosulfate concentrations were varied considerably to establish the character of the reaction. In the experiments reported in detail here the persulfate concentration was always made 0.01 M and the thiosulfate 0.02 *M*, these being the correct stoichiometric proportions; the main interest here lies in the catalytic effects, and with these concentrations the unimolecular law is followed closely over two-thirds of the reaction, except in certain solutions, as will be shown later. Suitable standard solutions of the salts used were pipetted from flasks in a large thermostat at 25° (±0.01°), thoroughly mixed and replaced in the thermostat. After suitable time intervals 50-cc. portions were withdrawn and titrated with a 30–40% alcoholic solution of iodine (about 0.01 M I_2) containing about 0.02 M potassium iodide. An aqueous solution containing more potassium iodide could not be used, since the persulfate oxidizes the iodide too rapidly during the titration; and from an aqueous solution 0.02 M in potassium iodide the iodine escapes too rapidly for accurate titration unless special precautions are taken.

The experiments using ordinary distilled water and redistilled water are listed in separate tables for comparison. It will be noted that the velocity in individual experiments is far different, but in spite of this the conclusions with regard to the catalytic effects are changed very little.

The velocity constants were obtained by plotting the logarithm (to the base 10) of the number of cc. of iodine used for the individual titrations, against the time in minutes; the slope of the straight line drawn through these points, multiplied by **2.303,** gives the velocity constant. In other words, $\log_{10} (a - x)$ is plotted against t in the equation

$$kt = 2.3 \log \frac{a}{a - x}$$

where a is the initial concentration of persulfate and $a - x$ the concentration at the time t, both expressed in cc. of iodine solution required. The value of k obtained is, of course, the same as if moles per liter of persulfate

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[7] Fales, "Inorganic Quantitative Analysis," The Century Co., New York, 1925.

were substituted; and the method does not even require standardization of the iodine solution. The logarithm of the initial titration is given, if desired, by the extrapolation of the straight line to zero time.

The reproducibility of these experiments is not high, but is, on the whole satisfactory when we consider the ease with which thiosulfate is oxidized and the anomalous character of the persulfate oxidations. It will be recalled that the velocity of the persulfate–oxalate oxidation catalyzed by silver ion is quite uncontrollable.[8] Here we have a very easily oxidized substance (thiosulfate) and a very active oxidizing agent (persulfate, capable even of oxidizing manganese salts to permanganate (with a catalyst)); the system is unstable and extremely sensitive to traces of catalysts. Consequently the highest degree of reproducibility cannot be expected.

1\. **The Uncatalyzed Reaction.**—An example of the actual titrations obtained is given in Table I.

TABLE I

DETAILS OF THE MEASUREMENTS IN ONE EXPERIMENT

0.01 M $K_2S_2O_8$; 0.02 M $Na_2S_2O_3$; redistilled water; 25°

Time, min.	0	165	295	445	555	675	800
Iodine, cc.	.	41.90	40.94	39.95	39.19	38.33	37.58

From the plot of log cc. I_2 vs. time, $k = 0.000177$.

Tables II and III summarize a number of experiments with ordinary distilled and redistilled water, and show the effect of an inert salt (potassium chloride) on the reaction velocity.

TABLES II AND III

SUMMARY OF RESULTS FOR THE UNCATALYZED REACTION

0.01 M $K_2S_2O_8$; 0.02 M $Na_2S_2O_3$; 25°

ORDINARY DISTILLED WATER			REDISTILLED WATER		
k, no. KCl	k, 0.02 M KCl	k, 0.06 M KCl	k, no. KCl	k, 0.02 M KCl	k, 0.06 M KCl
0.000357	0.000444	0.00132	0.000191	0.000262	0.000427
341	437	106	182	270	443
274	374			283	480
255	424			283	
262	460			263	
595	471			296	
606	733			287	
				293	

Discussion

Tables II and III show that the purity of the water has an enormous effect. The experiments in Table II are far from reproducible; this finally led to the use of redistilled water, and the experiments in Table III are much more concordant. Water redistilled in different stills, with glass or tin condensers, from ordinary distilled water from different sources, gave

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[8] King, THIS JOURNAL, 50, 2089 (1928).

fairly concordant results, and it is doubtful whether a very elaborate purification of the water would give much lower velocities. It is just possible that in absolutely pure water no reaction would occur, and that the reaction shown here is catalytic in character. Further experiments are in progress to establish this point.

Another observation from Tables II and III would agree with this. The salt effect is positive, abnormally high and with the ordinary distilled water at least, of an abnormal type—the salt effect increasing as the salt concentration increases. Now according to the well-substantiated theory of Bronsted, no unimolecular reaction could have a positive salt effect, since the salt effect is indicated in the equation

$$k = k_0F$$

where k is the observed velocity constant, k_0 the constant at zero ionic strength and F the "kinetic activity factor," in this case the activity coefficient of the reacting ion. F must decrease as the salt concentration is increased, at least in any usual case at low ionic strengths.

The same is true for a pseudo-unimolecular reaction between an ion and one or more neutral molecules present in constant concentration. The only kind of reaction which will satisfy the observations here is one between the persulfate ion and another negative ion present in constant concentration. A positive ion would mean a negative salt effect. The thiosulfate ion cannot be the negative ion, for its concentration is continually changing and the velocity is independent, or nearly independent of its concentration: The alternate conclusion is that the velocity-determining reaction is between the persulfate ion and an unknown, negative ion present in small amount as an impurity in the water. This mechanism seems untenable too, for the catalyst in ordinary distilled water is apparently some nearly nonvolatile substance and it seems improbable that such impurity would always be present in practically the same concentration in the redistilled water.

2. The Catalysis by Iodide Ion.—Since the persulfate–iodide oxidation

$$S_2O_8^{=} + 2I^- \longrightarrow 2SO_4^{=} + I_2$$

is much faster than the reaction

$$S_2O_8^{=} + 2S_2O_3^{=} \longrightarrow 2SO_4^{=} + S_4O_6^{=}$$

and the reaction between thiosulfate and iodine

$$2S_2O_3^{=} + I_2 \longrightarrow S_4O_6^{=} + 2I^-$$

is practically instantaneous, it is reasonable to expect that iodides will catalyze the oxidation of thiosulfate. If the mechanism of the catalysis is entirely as outlined above, it should be possible to measure the velocity of the persulfate–iodide reaction from the catalytic effect on the persulfate–thiosulfate reaction; the two should be additive. Since the iodide is regenerated as fast as it is used up, its concentration is constant, and the total reaction will be unimolecular in character. By subtracting the unimolecular constant for the uncatalyzed from that for the catalyzed reaction (at the same ionic strength), and dividing by the iodide concentration, we will obtain the himolecular constant for the persulfate–iodide reaction. This can then be compared with the persulfate–iodide constants determined directly with no thiosulfate present.

Similar examples of "induced catalysis" of this type are known, as the catalysis of the persulfate oxidation of phosphorous acid by iodide, measured by Federlin.[9] Here the reactions are

$$S_2O_8^{=} + H_3PO_3 + H_2O \longrightarrow 2SO_4^{=} + H_3PO_4 + 2H^+ \qquad (1)$$

$$S_2O_8^{=} + 2I^- \longrightarrow 2SO_4^{=} + I_2 \qquad (2)$$

$$H_3PO_3 + I_2 + H_2O \longrightarrow H_3PO_4 + 2I^- + 2H^+ \qquad (3)$$

and the net effect is similar, except that (3) is slower than the iodine–thiosulfate reaction; consequently, free iodine makes its appearance in the solution. Federlin concluded that the total rate of oxidation of phosphorous acid could be predicted exactly from the rates of the three reactions; as a mattter of fact, our examination of his data shows that the agreement is by no means good.[10]

In our experimental work we have two series of experiments in each of which the iodide-ion concentration is varied while the ionic strength is kept constant by suitable addition of potassium chloride to take the place of potassium iodide. The first series was run with both ordinary distilled and redistilled water, and it will be noticed that the persulfate–iodide constant is not much different, although the observed velocity is considerably different in the two cases.

Tables IV, V and VI give the results of these experiments. The total observed unimolecular constant is k; with no potassium iodide present, but potassium chloride to keep the ionic strength the same, $k_1 = k$. $k_2 = k - k_1$, i. e., k_2 is the increase in velocity constant caused by the potassium iodide; and k_3 is k_2 divided by the concentration of potassium iodide, i. e., the bimolecular persulfate–iodide constant in the presence of thiosulfate.

TABLE IV

SUMMARY OF EXPERIMENTS ON THE CATALYSIS BY IODIDE

0.01 M $K_2S_2O_8$; 0.02 M $Na_2S_2O_3$; 0.02 M (KCl + KI); ordinary distilled water; 25°; average value k_1 = 0.000435 (see Table II).

c_{KCl}	c_{KI}	k	k_2	k_3
0.016	0.004	0.00133	0.00090	(0.224)
.012	.008	.00179	.00135	.169
.010	.010	.00214	.00171	.171
.008	.012	.00242	.00198	.165
.004	.016	.00318	.00274	.171
.0	.02	.00399	.00355	.177
			Mean	0.171

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[9] Federlin, *Z. physik.* Chem., 41, 565 (1902).

[10] A similar example is given by Abel, *Z. Elektrochem.*, 14, 598 (1908).

TABLE V

SUMMARY OF EXPERIMENTS ON THE CATALYSIS BY IODIDE

Concentrations as in Table IV; redistilled water; value of k_1 used determined on same days as k (see Table III).

c_{KCl}	c_{KI}	k	k_3
0.016	0.004	0.000954	0.173
.016	.004	.000937	.163
.012	.008	.00158	.165
.012	.008	.00159	.162
.008	.012	.00227	.168
.008	.012	.00229	.166
.004	.016	.00294	.167
.004	.016	.00294	.167
.0	.02	.00361	.167
		Mean	0.166

The bimolecular constant k_3 is, within experimental error, the same over a considerable range of iodide concentration, and its value is changed but little by the use of ordinary distilled or redistilled water. Table VI shows the effect of a higher salt concentration on the velocity.

TABLE VI

SUMMARY OF EXPERIMENTS ON THE CATALYSIS BY IODIDE

0.01 M $K_2S_2O_8$; 0.02 M $Na_2S_2O_3$; 0.06 **M** (KCl + **KI); redistilled water;** 25°; **k_1 determined on same days as k (see Table III).**

c_{KCl}	c_{KI}	k	k_3
0.056	0.004	0.00125	0.203
.056	.OM	.00130	.205
.052	.008	.00209	.206
.052	.008	.00221	.216
.048	.012	.00294	.208
.044	.016	.00377	.207
.044	.016	.00372	.206
.04	.02	.00477	.216
		Mean	0.208

Discussion

From Tables V and VI it is seen that the salt effect on the persulfate–iodide reaction is positive, as is to be expected for **a** reaction between two ions of the same sign, and it is also normal in magnitude. We now come to the question of whether the velocities of the two slow reactions concerned are additive; *i.* e., whether the mechanism of the catalysis is as outlined above and the two independently measurable reactions with the one instantaneous reaction account for the observed velocity. A comparison of the persulfateiodide constant recorded here with constants recalculated from the data of Price on this reaction,[11] and measurements in this Labora-

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[11] **Price.** *Z. physik. Chem.*. 27, 474 (1898).

tory[12] led us to suspect that these constants were somewhat lower than the persulfate–iodide constants determined directly in solutions of the same ionic strength; however, the authors mentioned did not use solutions of exactly comparable composition. It is not always possible to compare velocities in solutions of the same ionic strength, even if the salts involved are of the same valence type, because of a considerable difference in specific salt effect, unless the concentrations are extremely low.

For this reason, a few experiments were made on this reaction in comparable solutions, replacing sodium thiosulfate with potassium sulfate, a salt of the same valence type. The constants were calculated from measurements made on the first one-fourth of the reaction, to avoid the complicating influence of the iodine formed (see previous work on this reaction). The results are recorded in Table VII.

TABLE VII

BIMOLECULAR CONSTANTS FOR THE PERSULFATE–IODIDE REACTION (NO THIOSULFATE PRESENT)

0.01 M $K_2S_2O_8$; 0.02 M K_2SO_4; redistilled water; 25°

c_{KCl}	c_{KI}	k_a
0.012	0.008	0.213
.008	.012	.216
.052	.008	.262
.048	.012	.268

As expected, these results show that the persulfate–iodide reaction, measured in the presence of thiosulfate, is several per cent. slower than when measured independently. This might be explained in one of three ways: (1) the specific salt effect of sodium thiosulfate is far different from that of potassium sulfate, which seems hardly probable; (2) the iodine–thiosulfate reaction is not as fast as supposed (which would keep the iodide concentration lower than that specified, and would necessitate the appearance of free iodine in the solution; this was never observed even with the aid of the starch test); or (3) one of the reactions, persulfate–iodide or iodine–thiosulfate, takes place in steps, resulting in the accumulation in solution of some colorless intermediate compound. This last seems possible, as both reactions are stoichiometrically trimolecular. We have, however, no way of testing this possibility. Two comments can be made: the agreement observed here is as good as that observed by Federlin in the case of the reaction mentioned before, and work in progress in this Laboratory shows that the velocity of the persulfate–iodide reaction is normal in the presence of extremely small concentrations of thiosulfate (10^{-5}–10^{-6} M).

3. The Catalysis by Copper Ion.—Price,'' in his early work on the persulfate–iodide reaction, found that the velocity was increased enormously by iron and copper salts. The work reported here shows that cop-

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[12] Jette and King, THIS JOURNAL, 51, 1048 (1929).

per salts have also an enormous effect on the persulfate–thiosulfate reaction. Price found a different catalytic effect of iron and copper salts in neutral and acid solution; both were fairly reproducible. Because of the decomposition of thiosulfate in acid solution most of our experiments were in neutral solution; a few, however, were carried out with a low concentration of acid present and are reported in the table.

It has been reported that traces of copper salts greatly accelerate the atmospheric oxidation of thiosulfates.[13] However, we believe this caused little error in the experiments reported here. A more important reaction which occurs in the system is that of cupric ion and thiosulfate.[14] Cupric ion is reduced to cuprous by thiosulfate, and negative complex ions of the type $Cu(S_2O_3)_y^{-x}$ are formed. The importance of this knowledge will be seen in the discussion.

If we assume that the cuprous copper is oxidized to cupric and instantly reduced by thiosulfate to cuprous again, we have a plausible mechanism for the catalysis. The relatively enormous catalytic effect is explained by the great speed of the persulfate–cuprous reaction. In this case again, by subtracting the constant of the uncatalyzed reaction (k_1), we obtain the part of the constant due to the copper catalysis, or, in other words, the constant of the persulfate–cuprous reaction. This reaction is pseudo-unimolecular, since the cuprous-ion concentration remains constant. On dividing this value by the copper-ion concentration, we obtain the bimolecular constant for the persulfate–cuprous reaction (k_4). The agreement of these constants as the copper-ion concentration is varied shows that this reaction is bimolecular, and gives a method of learning the velocity of this reaction, which cannot be measured directly as can the persulfate–iodide reaction.

With copper ion as the catalyst, there was a deviation from the unimolecular law, amounting to as much as 6 or 8% on the logarithmic plot when the reaction was half over. Hence a straight line was drawn as well as possible, tangent to the actual curve at zero time, and the slope of this line was taken as the best measure of the velocity in the first part of the reaction. The deviations were probably caused by the catalysis of side reactions; for instance, if the copper-ion concentration is high enough, sulfur is precipitated in the solution and the odor of hydrogen sulfide is apparent.

Since the copper-ion concentrations were so low, it was unnecessary to add varying amounts of another salt to keep the ionic strength constant. Experiments were run side by side with the catalyzed and uncatalyzed re-

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[13] See Hahn and Clos, *Z. anal. Chem.*, 79, 11 (1929).

[14] Mellor, Treatise on Inorganic and Theoretical Chemistry, Vol. X, p. 530; Dutoit, *J. chim. phys.*. 11, 650 (1913); Bassett and Durrant, *J. Chem. Soc.*, 123, 1279 (1923)

Tables VIII and IX

Summary of Experiments with Copper Ion as Catalyst

$0.01\ M\ K_2S_2O_8$; $0.02\ M\ Na_2S_2O_3$; 25°

Ordinary Distilled Water			Redistilled Water		
$C_{CuSO_4} \times 10^5$	k	k_4	$C_{CuSO_4} \times 10^5$	k	k_4
0	0.000595 $=k_1$	...	0	0.000191 $=k_1$	
0	.000606 $=k_1$	...	0	.000182 $=k_1$	...
2.5	.00926	347	2.5	.0114	449
1.25	.00471	329	1.25	.00602	466
0.5	.00232	318	0.5	.00244	449
.5	.00218	342	.25	.00135	462
.125	.00102	337	.25	.000771	464
.05	.000800	(410)	.125	.000335	(288)
.05	.000813	(414)			
				Mean	458
	Mean	334			

Tables X and XI

Summary of Experiments with Copper Ion as Catalyst

$0.01\ M\ K_2S_2O_8$; $0.02\ M\ Na_2S_2O_3$; $0.02\ M\ KCl$; 25°

Ordinary Distilled Water			Redistilled Water		
$C_{CuSO_4} \times 10^5$	k	k_4	$C_{CuSO_4} \times 10^5$	k	k_4
0	0.000471 $=k_1$	...	0	0.000283 $=k_1$	
2.5	.0114	436	0	.000283 $=k_1$	...
2.5	.0109	416	2.5	.0138	540
1.25	,00607	447	1.25	.00718	551
1.0	,00489	432	0.5	.00285	514
0.75	,00390	457	.25	.00166	540
.5	.00291	487	.25	.00155	517
.5	.00291	488	.125	.00100	513
.125	.00125	(624)	.05	.000549	532
			.0125	.000347	512
	Mean	452			
				Mean	527

Tables XII and XIII

Summary of Experiments with Copper Ion as the Catalyst

$0.01\ M\ K_2S_2O_8$; $0.02\ M\ Na_2S_2O_3$; $0.06\ M\ KCl$; 25°

Ordinary Distilled Water (From Two Sources)			Redistilled Water		
$C_{CuSO_4} \times 10^5$	k	k_4	$C_{CuSO_4} \times 10^5$	k	k_4
0	0.00132 $=k_1$	...	0	0.000509 $=k_1$	
1.25	.00887	604	0	.000503 $=k_1$	...
0.5	.00428	591	2.5	.0190	741
.125	.00214	655	1.25	.00966	732
			0.5	.00413	730
0	0.00106 $=k_1$	...	.5	.00400	698
2.5	.0162	605	.25	.00221	691
0.25	.00266	641	.25	.00227	704
.125	.00179	588	.05	.000869	721
			.0125	.000629	(969)
	Mean	614			
				Mean	717

TABLE XIV

THE EFFECT OF H^+ ON THE COPPER CATALYSIS

0.01 M $K_2S_2O_8$; 0.02 M $Na_2S_2O_3$; 0.02 *M* KCl; 1.25 × 10^{-5} M H_2SO_4; ordinary distilled water; 25°

$C_{CuSO_4} \times 10^5$	k	k_4
0	0.000733 = k	...
2.5	.0111	414
1.25	.00642	454
1.25	.00662	470
0.5	.00292	436
.25	.00191	470
	Mean	455

actions, to eliminate any effect from different samples of water. The results are given in Tables VIII–XIV.

Discussion

The constancy of the values of k_4 in each table indicates that we are actually measuring the velocity of a definite bimolecular reaction, which probably is, as suggested before, the oxidation of cuprous ion (in a negative complex with the thiosulfate ion) by persulfate. The tables show that in this case the character of the water used has an effect on the persulfate–cuprous reaction, though not as large as on the persulfate–thiosulfate reaction. The salt effect is positive, in complete agreement with the belief that the velocity-determining reaction is between two negative ions. The effect of hydrogen ion is curious; although it increases the velocity of the persulfate–thiosulfate reaction a great deal, its effect on the persulfate–cuprous reaction is negligible. Although cupric ion would be considerably hydrolyzed in pure water solution, evidently in the thiosulfate solution the copper ion is all in the same form whether H^+ is present above its normal value in water or not. This is different from the effect of copper salts on the persulfate–iodide reaction; Price found that acids had a considerable effect on the velocity, presumably because they decrease hydrolysis of the copper ion. Price's data show considerable variation in the value of the persulfate–cuprous constant, chiefly because the straight line obtained by plotting copper-ion concentration against increased velocity constants does not extrapolate to zero effect at zero concentration for some reason.

Inspection of Price's results shows that copper ion does not have as great an effect on the persulfateiodide reaction as on the persulfate–thiosulfate reaction; 0.0025 M copper ion increases the velocity three to five times in the former case, very much more in the second. The mechanism of the catalysis in the two cases is different; in the first the copper is probably kept in the form of positive cupric ion, in the second by the extremely rapid reaction with thiosulfate, in the form of negative cuprous complex ion.

A point worthy of interest is the possibility of measuring the velocity of extremely rapid reactions by such a catalytic method as this. The iodide catalysis shows that the assumption of additive velocities is not far from true, and, if the same is true in the copper catalysis, we have a means of ascertaining, roughly at least, the velocity of a reaction up to 1000 times as fast (for equal concentrations) as those easily measured by the usual means. Direct measurement of such velocities can be accomplished only by some such scheme as that of Hartridge and Roughton,[15] used later by Saal[16] and by La Mer and Read.[17]

4. The Combined Catalysis by Iodide and Copper Ions.—The addition of both copper and iodide ions to the persulfate–thiosulfate system presents interesting possibilities. Price studied the effect of both copper and iron ions together on the persulfate–iodide reaction and found that the two together had practically twice the catalytic effect calculated from adding their separate effects. He was unable to explain this, except rather vaguely as a "promoter" effect.

There is a possibility in this system of at least six reactions, some measurable, some immeasurably fast.

(1) The persulfate–thiosulfate reaction
(2) The persulfate–iodide reaction } measured before
(3) The persulfate-cuprous reaction
(4) The thiosulfate-cupric reaction } "instantaneous"
(5) The thiosulfate–iodine reaction
(6) The cupric–iodide reaction very fast

The copper salt may catalyze the persulfate–iodide reaction, and so increase the effect of the iodide on the persulfate–thiosulfate reaction; or the iodide may catalyze the persulfate–cuprous reaction, through Reaction 6, and hence increase the effect of the copper salt on the persulfate–thiosulfate reaction; *i. e.*, if the iodide can complete its cycle of iodide–iodine–iodide through the path of Reactions 6–5 faster than through Reactions 2–5, or the copper can complete its cycle cuprous–cupric–cuprous faster through Reactions 3–6 than through Reactions 3–4, there will be an unusually large catalytic effect.

By a process similar to that used in the last section, from a suitable number of experiments we can obtain the constant for either Reaction 2 or 3 in this mixed solution, and compare it with those obtained before. To obtain the most concordant results, it was found necessary to run all experiments used in these calculations simultaneously, since, in general, the velocity constants were reproducible on the same day, with the same materials, but might vary 5–10% on different days. Consequently, experiments were run with no copper or iodide, some with copper, some with io-

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[15] Hartridge and Roughton, *Proc. Roy. Soc.* (London), **104A,** 376 (1923); *Proc. Cambridge Phil. Soc.,* **23,** 450 (1926).

[16] Saal, *Rec. trav. chim., 47,* **73,** *264,* 385 (1928).

[17] La Mer and Read, THIS JOURNAL, **52,** 3098 (1930).

TABLE XV

EXPERIMENTS WITH BOTH IODIDE AND COPPER IONS AS CATALYSTS

0.01 M $K_2S_2O_8$; 0.02 M $Na_2S_2O_3$; 0.02 *M* (KCl + KI); redistilled water; 25°.

$c_{\mathrm{CuSO_4}} \times 10^5$	c_{KCl}	c_{KI}	k	k_3	k_4
0	0.02	0	0.000287 = k_1	...	...
			.000293 = k_1	...	...
0	.016	0.004	.000937	0.162	...
0	.012	.008	.00159	.162	...
0	.008	.012	.00229	.166	...
1	.02	0	.00555	...	526
1	.016	.004	.00654	.241	560
1	.012	.008	.00724	.214	565
1	.008	.012	.00840	.239	610
0.75	.02	0	.00432	...	538
.75	.016	.004	.00498	.163	538
.5	.02	0	.00297	...	537
			.00289	...	518
.5	.016	.004	.00380	.206	571
.5	.012	.008	.00443	.193	568
.5	.008	.012	.00527	.198	594
.375	.02	0	.00233	...	546
			.00226	...	578
.375	.016	.004	.00313	.198	584
.375	.012	.008	.00385	.191	604
.375	.008	.012	.00461	.196	618
.25	.02	0	,00170	...	556
			.00162	...	529
.25	.016	.004	.00244	.191	602
.25	.012	.008	.00317	.194	632
.25	.008	.012	.00386	.187	625
.125	.02	0	.000980	...	564
.125	.016	.004	.00176	.194	657

TABLE XVI

EXPERIMENTS WITH BOTH IODIDE AND COPPER IONS AS CATALYSTS. HIGHER IONIC STRENGTH

0.01 M $K_2S_2O_8$; 0.02 M $Na_2S_2O_3$; 0.06 M (KCl + KI); redistilled water; 25°

$c_{\mathrm{CuSO_4}} \times 10^5$	c_{KCl}	c_{KI}	k	k_3	k_4
0	0.06	0	0.000480 = k_1	...	...
0	.056	.004	.00130	0.205	...
0	.052	.008	.00221	.216	...
0.5	.06	0	.00413	...	730
.5	.056	.004	.00512	.246	763
.5	.052	.008	.00615	.252	788
.375	.06	0	.00333	...	761
.375	.056	.004	.00421	.219	776
.375	.052	.008	.00533	.249	834
.25	.06	0	.00221	...	691
.25	.056	.004	.00325	.261	782
.25	.052	.008	.00421	.250	801

dide and some with both, on the same day. Tables XV and XVI show the results of these experiments: k is again the total observed unimolecular constant; k_1 the constant with no catalyst present; k_3 the persulfate–iodide constant, obtained by subtracting k with copper but no iodide present from k with iodide and the same copper-ion concentration and dividing the difference by the iodide-ion concentration. Again, k_4 is the constant of the persulfate–cuprous reaction, obtained by subtracting k with iodide and no copper ion present from k with copper ion present and the same iodide concentration and dividing the difference by the copper-ion concentration.

Discussion

It will be noticed that in these mixed solutions the values of the persulfate–cuprous constants and of the persulfate–iodide constants are not as concordant as in the previous experiments with simpler solutions. This is to be expected since the experimental errors are greater, and the more catalytic effect, the greater the deviation from the unimolecular law for individual reactions (however, the deviation of points in the logarithmic plot never exceeded 8% when the reaction was half over). One consistent variation seems to be that the catalytic effect of the copper, per mole of copper salt, increased with decreasing copper-ion concentration. This is difficult to explain, but is exactly what Price found in the copper-ion catalysis of the persulfate–iodide reaction. When the catalytic effect is plotted against copper-ion concentration, the straight line found does not extrapolate to zero effect for zero concentration.

In these solutions it will be noticed that the persulfate–iodide constant is increased practically to the normal value (see Table VII). We cannot tell whether this is because the additional catalytic effect of this small copper-ion concentration is just sufficient in these solutions to bring the value up fortuitously, or whether the copper prevents some other reaction which has an inhibiting effect on the persulfate–iodide reaction. However, there is by no means the same catalytic effect of copper ion on the persulfate–iodide reaction that would be found if thiosulfate were absent; while there is undoubtedly some effect of the iodide on the persulfate–cuprous reaction, it is not large; there is no large unexplained "promoter" effect such as Price found with two catalysts present. In other words, only few if any copper and iodide ions go through the alternative cycles discussed at the beginning of this section.

5. The Effect of a Non-electrolyte (Cane **Sugar)** on the **Velocity.**—Several attempts have been made in recent years to correlate the effect of non-electrolytes on the velocity of ionic reactions, without a high degree of success. If the effect of the non-electrolyte were merely to change the activity coefficients of the reacting ions, then we should be able to make predictions. From the expression

$$\ln f = z^2 \frac{e^2}{2DkT}\sqrt{\frac{4\pi e^2 nz^2}{DkT}}$$

we see that any change in D, the dielectric constant, caused by a non-electrolyte should show a corresponding change in f; in fact

$$\ln f \sim \frac{1}{D^{3/2}}$$

With regard to "neutral salt effect" on ionic reaction velocities, there is no doubt that the activity coefficient is all-important, but the effect of non-electrolytes is by no means merely that of changing the activity coefficients.

By measuring the effect of a non-electrolyte on the persulfate–thiosulfate reaction alone and in the presence of iodide, we can also find the effect on the persulfate–iodide reaction. The latter has been measured before in solutions containing no thiosulfate; hence we can compare the effect in the two cases.

The experimental methods were the same as before. Ordinary distilled water was used, hence Table XVII should be compared with Table IV.

TABLE XVII

THE EFFECT OF SUCROSE ON THE CATALYZED AND UNCATALYZED REACTION

0.01 M $K_2S_2O_8$; 0.02 M $Na_2S_2O_3$; **ordinary distilled water;** 25°.

c_{Sucrose}	c_{KCl}	c_{KI}	k	k_3
0	0	0	0.000255	
0.35	0	0	.000390	
.70	0	0	.000818	
1.05	0	0	,00120	
0	0 02	0	.000460	
0.35	.02	0	.000620	
.70	.02	0	.00102	
1.05	.02	0	,00142	
0.35	.012	0.008	.00229	0.207
.35	.006	.014	.00348	.203
.35	0	.02	.00469	.203
.70	.012	.008	00308	.263
.70	.006	.014	.00444	246
.70	0	.02	00576	.238
1.05	.012	.008	.00341	.249
1 05	.006	.014	.00493	.250
1.05	0	.02	.00633	.240

Discussion

The constants for both the persulfate–thiosulfate and the persulfate–iodide reactions are increased by the cane sugar; this agrees with the work of Kiss and Hatz[18] on the persulfate–iodide reaction above.

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[18] **Hatz,** *Magyar Chem. Folyoirat, 34,* 141, 154, 177 (1928); C. *A.*, 23,4872 (1929); **Kiss and Hatz,** *Rec. trav. chim., 48,* 7 (1929).

For these reactions it was noticed that the presence of sugar caused deviations from the unimolecular curve; with the highest sugar concentrations the reaction was practically of zero order over two-thirds of its course. Hence many of the constants in the table were determined on this basis. When iodide is present, however, the curve again becomes unimolecular, as the persulfate–iodide reaction is pseudo-unimolecular and much faster than the uncatalyzed reaction.

It can be seen from the table that the effect of the sugar on the persulfate–iodide reaction appears to have reached a maximum between 0.7 M and 1.05 M concentrations. This is far different from the results reported by Kiss on the direct reaction, where the sugar has an increasingly greater effect up to a concentration of one molar. The presence of the thiosulfate has apparently modified the character of the reaction.

It is difficult to draw any general conclusions with respect to the effect of the non-electrolyte. For the persulfate–iodide reaction Kiss found that sugar and urea increase the velocity, while methyl and ethyl alcohols and glycerol decrease it. In all these cases the dielectric constant of the medium is decreased; hence the effect is more than that of change in dielectric constant on the activity coefficients.

6. Catalysis by Iron and Silver Salts.—It is well known that ferric salts oxidize thiosulfates, being thereby reduced to ferrous; and that ferrous salts are rapidly oxidized to ferric by persulfate. Hence it might be expected that iron salts would catalyze the persulfate–thiosulfate reaction. Unfortunately it is difficult to run suitable experiments since ferric or even ferrous salts are considerably hydrolyzed in neutral solution; if the solution is acid enough to control this hydrolysis and prevent precipitation of ferric hydroxide, the thiosulfate decomposes too rapidly. The first titrations in a few experiments showed that iron salts are not as effective catalytically as copper salts.

It may be of interest to discuss the similar iron salt catalysis of the persulfate–iodide reaction. The rate of the extremely rapid oxidation of ferrous ion by persulfate ions has been measured directly by Saal.[19] His method of expressing concentrations is obscure and apparently burdened with typographical errors, but if we have interpreted correctly, for a solution containing 0.0005 M $S_2O_8^=$, 0.0005 M Fe^{++}, 0.01 M H^+, 0.1 *M* KCl, at 12.8°, the bimolecular constant for the reaction is approximately 2000.[20] At a lower salt concentration and 25°, to compare with the work of Price on iron salt catalysis of the persulfate–iodide reaction, this value would be increased to perhaps 5000. It is difficult to calculate the velocity of the persulfate–ferrous constant from Price's data; the persulfate–iodide re-

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[19] Saal, Rec. trav. *chim.*, 47, 385 (1928).

[20] Recalculated according to the scale used here from the equation $(-dC_{S_2O_8^=})/dt = kC_{S_2O_8^=}C_{Fe^{++}}$, with concentrations in moles per liter and t in minutes.

action is bimolecular, and if the catalysis by ferrous ion follows the mechanism

$$S_2O_8^{=} + 2Fe^{++} \longrightarrow 2SO_4^{=} + 2Fe^{+++} \qquad (1)$$
$$2Fe^{+++} + 21- \longrightarrow 2Fe^{++} + I_2 \qquad (2)$$

Reaction **1** will be pseudo-unimolecular if it is the velocity-determining reaction; if **(2)** is the slower, velocity-determining reaction, it will be pseudo-unimolecular.

Assuming that **(1)** is the velocity-determining reaction the velocity equation becomes

$$-\frac{dC_{S_2O_8^{=}}}{dt} a\ k_1C_{S_2O_8^{=}}\ C_{I^-} + k_2C_{S_2O_8^{=}}$$

where k_1 is the velocity constant of the uncatalyzed reaction; $k_2 = k_3C_{Fe^{++}}$, and k_3 is the bimolecular velocity constant of the persulfate–ferrous reaction.

From Price's data, for a solution containing **0.00625 M $S_2O_8^{=}$, 0.025 M I–, 0.005 *M* H+, 25°,** we obtain the value **0.147** for k_1. For the same solution +0.00025 M Fe^{++}, by reading $-dC_{S_2O_8^{=}}/dt$ from the plotted curve and using the above value of k_1, we calculate for k_3 values ranging from **65** to **40** during the course of the reaction. The complete lack of agreement with the work of Saal indicates that the above mechanism is incorrect; perhaps Reaction **2** is the velocity-determining reaction. If so, values not far different from these above **(40–65)** become the bimolecular constants for the reaction

$$2Fe^{+++} + 2I^- \longrightarrow 2Fe^{++} + I_2$$

In any case, the mechanism of this and similar catalytic reactions is far from clear.

Silver nitrate was also tried as a catalyst, since silver salts are so effective in other persulfate oxidations. However, it was not a good catalyst; the trivalent silver compound described by Yost and others[21] precipitated even with low silver-ion concentrations, and the catalysis was not very great.

Summary

The velocity of the reaction

$$S_2O_8^{=} + 2S_2O_3^{=} \longrightarrow 2SO_4^{=} + S_4O_6^{=}$$

has been measured, **(1)** alone, **(2)** with iodide ion as a catalyst, (3) with copper ion as a catalyst, **(4)** with both iodide and copper ions as catalysts in a mixed solution and **(5)** in the presence of cane sugar with and without iodide ion as a catalyst.

From these measurements, certain observations about the nature of the several reactions involved have been made.

1. The uncatalyzed reaction is pseudo-unimolecular or nearly so, *i.* e., independent to a great extent of the thiosulfate concentration; but the salt

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[21] Yost, Tars JOURNAL. 48, 374 (1926).

effect indicates the velocity-determining reaction to be between two negative ions.

2. From the iodide catalysis can be calculated a constant for the bimolecular persulfate–iodide reaction; this constant is some 20–30% lower than when the velocity is measured independently, at least in solutions containing 0.02 *M* thiosulfate.

3. From the copper catalysis a constant can be calculated for the persulfate–copper ion reaction; the salt effect on this catalysis shows that the persulfate–copper ion reaction is between two negative ions, as might be expected from the fact that Cuff is reduced and changed into a negative complex cuprous ion by thiosulfate.

4. The effect of sugar is to increase the velocity of the persulfate–thiosulfate reaction, and to increase the velocity of the persulfate–iodide reaction in the presence of thiosulfate in a somewhat abnormal fashion.

Further work on this reaction is in progress.

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A POTENTIOMETRIC STUDY OF ACID-BASE TITRATION SYSTEMS IN THE VERY STRONGLY ACID SOLVENT FORMIC ACID[1]

BY LOUIS P. HAMMETT AND NICHOLAS DIETZ, JR.

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If the ionization of an acid depends upon a reaction of the type

$$HCl + OH_2 \rightleftharpoons OH_3^+ + Cl^-$$

then the effect of the solvent upon the acidity of the solution obtained and upon the extent of the ionization may conveniently be separated into two factors.[2] One of these may be represented as the inherent basicity of the solvent and acts in such a way that a decreased basicity decreases the ionization of the acid but increases the acidity of the solution because the ionization takes place only as a result of the transfer of a proton from a weaker to a firmer binding. Thus hydrochloric acid is a strong electrolyte in water, but is only incompletely ionized in formic acid.[3] Nevertheless, indicator experiments show that the solution in formic acid is more acid than that in water. It is clear that the properties of a base should depend upon the acidity of the solvent in analogous fashion.

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[1] This article is based upon a dissertation submitted by Nicholas Dietz, Jr., to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1930.

[2] Hammett, THIS JOURNAL, 50, 2666 (1928).

[3] (a) Schlesinger and Calvert, *ibid.*, 33, 1924 (1911); (b) Schlesinger and Martin, *ibid.*, 36, 1589 (1914).

The other factor is a medium effect which may be represented as the result of changes in ionic activity coefficients, that is, in the interionic electrical forces. A change in medium resulting in an increase in these forces results in a decreased ionization but probably in no great change in true acidity. Thus a solution of hydrogen chloride in ether is much less ionized than one in water. Basic indicators show decreased, acid indicators increased, acidity. It may further be expected that solvents of low dielectric constant, in which these forces seem always to be large, should exhibit large and specific salt effects. That is, relatively dilute electrolyte solutions in such a solvent should exhibit the same kind of complicated behavior as do very concentrated aqueous solutions. The potentiometric studies of Hall and Werner[4] on acetic acid solutions of bases seem to show this sort of effect in a pronounced degree.

It has seemed desirable to test further this point of view by the investigation of the properties as a solvent for acids and bases of a substance which is less basic and more acidic than water but which has the high dielectric constant and generally high solvent power for salts which may be taken to indicate interionic forces of relatively small magnitude.

We have therefore investigated potentiometrically solutions of acids and bases in formic acid. This solvent has a dielectric constant of 62.0 at 15°, it is a solvent for many salts,[5] including sodium and potassium chlorides; which have a very low solubility in most organic solvents, and solutions of salts give cryoscopic and conductivity values which correspond to extensive dissociation.[6] In these respects formic acid is much more like water than is such a solvent as acetic acid, in which salts give cryoscopic effects indicating association rather than dissociation[5] and conductivity dilution curves with maxima and minima. With respect to acidity and basicity, however, formic acid differs greatly from water, and solutions in it are even more deserving of the term superacid than are those acetic acid solutions in which Hall and Conant[7] did their pioneer work on the potentiometric investigation of strongly acid solvents. There is further interest in the potentiometric investigation of this solvent because of the existence of the precise and thorough conductivity studies of Schlesinger and his co-workers.[3,6]

In contrast the solvent offers considerable experimental difficulties. Solutions cannot be made anhydrous by the addition of an anhydride. The pure liquid decomposes slowly, and this decomposition is hastened by the presence of strong acids. We have found it impossible in spite of

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[4] Hall and Werner, THIS JORNAL, 50, 2367 (1928).

[5] Zanninovich-Tessarin, *Z. physik. Chem.*, 19,251 (1898).

[6] References 3 and 5, also (a) Schlesinger and Coleman, THIS JOURNAL, 38, 271 (1916); (b) Schlesinger and Mullinix, *ibid.*, 41, 72 (1919); (c) Schlesinger and Reed, *ibid.*, 41, 1921 (1919); (d) Schlesinger and Bunting, *ibid.*, 41, 1934 (1919).

[7] Hall and Conant, *ibid.*, 49, 3047 (1927).

very considerable investigation and the preparation of electrodes of a wide range of catalytic activity to obtain reliable hydrogen electrode potentials. Duplicate electrodes failed to agree and all electrodes adjusted themselves very slowly to changes in hydrogen-ion concentration. Nevertheless several titration curves were obtained with breaks qualitatively similar to those obtained with quinhydrone electrodes. Entirely satisfactory results were obtained with the *p*-benzoquinhydrone electrode. Even here, however, greater pains were necessary in the selection of electrodes than is the case in aqueous solutions, and it was necessary, moreover, to carry out measurements within a fairly short time interval because the potentials were found to drift in a negative direction (that is, in the direction of reduction) in acid solutions. Chloranil and 1,4-naphthoquinone were tried as substitutes for the benzoquinone, the former because it has no nuclear hydrogen and because it has been recommended by Conant and Hall for use in acetic acid solutions; the latter because it has a lower oxidation potential than benzoquinone. Chloranil seemed somewhat inferior to benzoquinone in definiteness and reproducibility. The behavior of the naphthoquinhydrone system is greatly affected by small variations in the method of preparation of the quinhydrone from the quinone. Some preparations gave results which were greatly superior to benzoquinone in reproducibility and freedom from drift in acid solutions, others were very inferior.

The method of investigation consisted in carrying out potentiometric titrations. Benzene sulfonic acid was found to be a suitable strong acid, as was expected from Hantzsch's indicator experiments. Sodium salts are in general strong electrolytes, and sodium formate if it is a strong electrolyte must have the greatest base strength possible in this solvent. As a reference half-cell we used a purely arbitrary constant system, and as a salt bridge a solution saturated with the very soluble sodium benzene sulfonate. There is of course no reason to believe that this bridge reduced the junction potential to zero, but it seems entirely probable that it should decrease to a small value the variation in contact potential with not too great changes in composition of the solution being titrated. The validity of the assumption seems justified by the results, as was the case with the similar scheme of Hall and Werner in acetic acid solutions.[4]

Materials

Formic Acid.—Kahlbaum 100% formic acid was first distilled in vacuo; the distillate was then purified by the method described by Coolidge.[5] The most highly purified acid had a melting point of 8.24°. The corresponding value obtained by Coolidge after more prolonged purification was 8.26°. The melting point was determined with the usual precautions, using a thermometer which was carefully compared with one recently calibrated by the Bureau of Standards. The purified acid was carefully pro-

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[5] Coolidge, THIS JOURNAL. 50, 2166 (1928).

tected from moisture and kept at a temperature of 10" to decrease the rate of decomposition. The purest acid (melting point **8.23** to 8.24°) was used for the titration cell solutions. Less highly refined acid (melting point **8.21** to **8.22")** was employed in the bridge and in the reference cell. Although formic acid is hygroscopic, it is not extraordinarily so: for example, a sample with a melting point of **8.05"** was freely exposed to the atmosphere for thirteen minutes, after which the melting point had not changed measurably.

Sodium Formate.—The Kahlbaum salt was used after careful drying. Analysis by conversion to sodium sulfate gave a figure of **99.9%.**

Benzene Sulfonic Acid.—After considerable difficulty with purchased material we made this substance by the method described by Fierz[9] for toluene sulfonic acid with excellent results. The aqueous solution after removal of sulfuric acid was evaporated to a sirup and then dehydrated and distilled at a pressure of **0.01** to **0.001** mm.[10] The white crystalline product was again distilled in a special apparatus, under the full vacuum of a diffusion pump with a liquid-air trap, and at a temperature of 120°, directly into glass bulbs, **10** to 15 mm. in diameter, which were then sealed off. By titration against sodium hydroxide free from carbon dioxide and standardized with Bureau of Standards benzoic acid it was found to have a purity of **99.7** to **99.9%.** The anhydrous sulfonic acid is extremely hygroscopic. In preparation for a titration, a weighed bulb was broken in a dry mortar, and solution of the sulfonic acid in formic acid, which does not take place very rapidly, was allowed to proceed in the shelter of a desiccator kept dry with phosphorus pentoxide. After rinsing with formic acid, the glass fragments were collected and weighed.

Urea.—The sample melted at **133°.**

Triphenyl Carbinol.—The Eastman Kodak product was used. It melted at 162.5°.

Benzoquinhydrone.—The Eastman Kodak product melting at **170–171°** was used.

Apparatus and Method

The pyrex cell employed is illustrated in Fig. 1. It was found to be compact and convenient in use, and mixing of the solutions was avoided without the introduction of too great electrical resistance.

The electrodes were in most cases gold film burned on glass from a concentrated solution of pure gold chloride in glycerin containing a little oil of lavender. Electrical connection was established by a strip of platinum foil fused through the end of the glass tube which served as support. Before use they were cleaned with chromic acid, washed and heated to dull redness. Such electrodes gave very reproducible results, and readjusted themselves rapidly upon addition of acid or base. Electrodes of pure gold wire were found to give equally satisfactory results. Platinum electrodes were very unsatisfactory, showing differences of potential in a single solution of several millivolts. Gold plated platinum electrodes were no improvement upon bare platinum. This is in agreement with the observation frequently made in this Laboratory that platinum is particularly prone to contain electromotively active impurities. It is not clear, however, why these differences are so much greater in formic acid solutions than in aqueous ones. Two electrodes were always used in both titration and reference half-cells, and were frequently checked against each other during the course of the titration. The agreement obtained was approximately **0.1** millivolt.

In preparation for a titration, the salt bridge solution, consisting of formic acid saturated with sodium benzene sulfonate and carrying excess solid salt in suspension,

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[9] "Grundlegende Operationen der Farbenchemie," Zurich, 1920, p. **190.**

[10] The smaller apparatus described in the leaflet, "Synthetic Organic Chemicals," Vol. II, No. 3, issued by the Eastman Kodak Company, February, **1929,** was used.

was introduced through a funnel into the salt bridge. The glass plugs were then firmly put into place with tongs, leaving a film of conducting solution around the sides of each plug. The excess solution squeezed out into the half-cells by this procedure was removed and the half-cells were rinsed several times with formic acid.

The solution to be titrated and the reference solution were then introduced into their respective half-cells. The reference solution consisted of formic acid saturated with sodium benzene sulfonate and containing 0.098 molar sodium formate. Quinhydrone was then added to both half-cells until an appreciable excess remained. Rough measurements indicated that the solubility of benzoquinhydrone in formic acid is about 0.1 molar. hi

Quinhydrone reacts slowly with formic acid in the presence of benzene sulfonic acid, the reaction being evidenced by a change in color with eventual formation of tarry products, and by a drift in potential toward less positive values. There was, however, no evidence of such reaction in sodium formate solutions, which are, of course, basic with respect to the solvent formic acid. For this reason titrations were started in basic solution, the reference half-cell solution was basic, and the titrations were completed within a time which experience showed would prevent a serious change in the potentials on the acid side of the end-point. The rate of potential drift was found to be 0.1 millivolt per minute in a 0.1 molar sulfonic acid solution, and not more than 0.01 millivolt per minute in a 0.025 molar sulfonic acid solution.

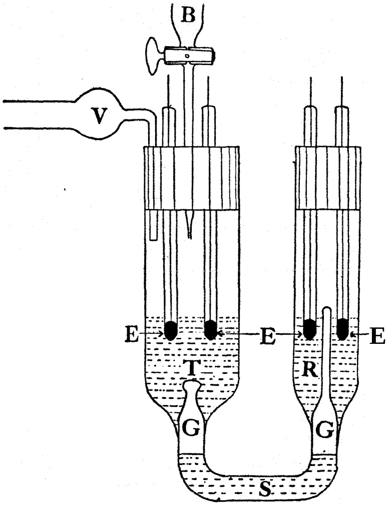

Fig. 1.—Titration cell. T, titration half-cell; R, reference half-cell; S, salt bridge; G, ground-glass plugs; E, electrodes; B, buret; V, vent.

Before use all glassware was thoroughly baked at 110° and was stored over phosphorus pentoxide or otherwise protected from moisture. In use the vent of the cell and the opening of the buret were protected by tubes containing pentoxide.

All measurements were made at a temperature of 25.00°, maintained by immersion of the cell in a Freas water thermostat. A properly calibrated potentiometer and standard cell and a galvanometer with a sensitivity of 2602 megohms gave the electrical measurements a precision of one to two-tenths of a millivolt with the highest resistance cells used.

Sodium Formate Titrations.—In Tables I, II and III are listed the data for titrations by the above described method of various concentrations of sodium formate against benzene sulfonic acid. Under C_b are calculated the concentrations of sodium formate not neutralized, under C_a the concentrations of benzene sulfonic acid in excess of that required to neutralize the sodium formate. The calculations assume a simple and complete neutralization, volume additivity, and a specific volume of dissolved quinhydrone equal to that of the solid substance. The values in the column headed pK are calculated by the equation

$$pK = \frac{E_{ab}}{0.0591} - \log C_aC_b$$

TABLE I

TITRATION DATA

Sodium formate: benzene sulfonic acid (p-benzoquinhydrone electrodes). 0.001991 mole of sodium formate used (= 15.40 cc. of 0.1294 molar sodium formate); 0.4751 molar = titer of benzene sulfonic acid; 4.19 cc. of benzene sulfonic acid = theoretical end-point.

Add added, cc.	X = fraction of base neut.	$E_{obs.}$, volt	E, volt, corr. to const. vol.	C_b	pK (ref. to C_a = 0.02482)
0	0	0.0252	0.0252	0.1294	5.425
0.31	0.074	.0262	.0267	.1174	5.451
1.13	.270	.0300	.0318	.0880	5.512
2.06	.492	.0367	.0399	.0580	5.579
2.96	.707	.0470	.0515	.03184	5.666
3.13	.747	.0498	.0546	.02718	5.688
3.31	.790	.0557	.0607	.02236	5.672
3.53	.843	.0627	.0681	.01657	5.684
3.67	.876	.0677	.0733	.01296	5.706
3.84	.917	.0781	.0839	.00865	5.705
3.98	.950	.0913	.0973	.00515	5.708
4.13	.986	.1162	.1224	.00146	5.833"
				C_a	pK (referred to C_b = 0.002718)
4.30	1.027	0.1450	0.1514	0.00265	5.753"
4.44	1.060	.1623	.1689	.00599	5 692
4.73	1.129	.1828	.1898	.01275	5.711
5.27	1.258	.1985	.2061	.02482	5.688
5.83	1.392	.2081	.2165	.0367	5.680
6.79	1.621	.2170	.2265	.0557	5.655
					Average 5.646

[a] Omitted in the average because of proximity to the end-point.

TABLE II

TITRATION DATA

0.001216 mole of sodium formate used (= 16.3 cc. of 0.07460 molar sodium formate); 0.4611 molar = titer of benzene sulfonic acid: 2.64 cc. = theoretical end-point.

Acid added, cc.	X = fraction of base neut.	$E_{obs.}$, volt	E, volt, corr. to const. vol.	C_b	pK (referred to C_a = 0.00860)
0	0	0.0374	0.0374	0.07460	5.657
0.45	0.171	.0403	.0410	.06021	5.701
1.64	.621	.0538	.0563	.02567	5.842
2.14	.811	.0713	.0745	.0125	5.858
2.62	.993	.126	.1299	.0005	6.34[a]
				C_a	pK (referred to C_b = 0.02567)
2.79	1.057	0.160	0.1641	0.00362	5.827[a]
3.00	1.136	.183	.1874	.00860	5.842
3.71	1.406	.2043	.2096	.02466	5.746
4.92	1.864	.2186	.2254	.04954	5.684
6.97	2.640	.2293	.2385	.08580	5.626
					Average 5.730

[a] Omitted in the average.

TABLE III

TITRATION DATA

0.0004367 **mole sodium formate used** (= 19.70 **cc. of** 0.02217 **molar sodium formate);** 0.4374 **molar = titer of benzene sulfonic acid;** 0.998 **cc. = theoretical end-point.**

Acid added, cc.	X = fraction of base neut.	$E_{obs.}$, volt	E, volt. corr. to const. vol.	C_b	pK (referred to $C_a = 0.00489$)
0	0	0.0706	0.0706	0 02217	5.788
0.309	0.310	.0761	.0765	.01507	5.862
.610	.611	.0912	.0920	.00836	5.862
.702	.703	.0980	.0990	.00635	5.867
.817	.819	.1096	.1107	.00386	5.886
.906	.908	.1238	.1250	.00195	5.942[a]
				C_a	pK (referred to $C_b = 0.00836$)
1.001	1.003	0.1417	0.1430	0.00042	5.304[a]
1.116	1.119	.1657	.1671	.00248	5.945
1 232	1.235	.1783	.1799	,00489	5.862
1.375	1.376	.1892	.1908	.00782	5.842
1.475	1.478	.1961	.1980	.00985	5.859
1.638	1.641	.2031	.2052	.01312	5.853
1.852	1.856	,2095	.2118	.01733	5.841
2.071	2.075	.2141	.2167	.02156	5.823
2.403	2.408	.2189	.2218	.02781	5.795
2805	2.811	.2229	.2263	.03511	5.761
3.099	3 106	.2251	.2289	.0403	5.738
3.545	3.552	.2276	.2319	.0479	5.705
				Average	5.828

[a] **Omitted in the average.**

where E_{ab} is the observed difference in potential between a point on the acidic side and another point on the basic side of the titration end-point, all points on the basic side being referred to a single point (given in the heading of the column) on the acidic side, and all points on the acidic side being referred to a single point on the basic side. C_a is the concentration of sulfonic acid at the acid point and C_b the concentration of sodium formate at the basic point.

If the liquid junction potential remains constant during the titration, and if benzene sulfonic acid and sodium formate are completely ionized

$$E_{ab} = 0.0591 \log \frac{C_a f_a}{C_{ab} f_{ab}}$$

where C_{ab} is the concentration of hydrogen ion (probably $H_3CO_2^+$) in a solution of formate ion concentration C_b, f_{ab} is the activity coefficient of hydrogen ion in the same basic solution, and f_a is the activity coefficient of hydrogen ion in a solution of benzene sulfonic acid of concentration C_a. It follows that

$$pK = \frac{E_{ab}}{0.0591} - \log C_a C_b = -\log C_a C_b \frac{f_{ab}}{f_a}$$

With complete dissociation C_b is the concentration of formate ion in the basic solution, and C_{ab} is the hydrogen ion concentration of the same solution. The radio f_{ab}/f_a is nearly one, since it is the ratio of the activity coefficients of a given ion in two solutions of approximately the same total ion concentration. The quantity pK is therefore the negative logarithm of the product of the concentrations of the ions of the solvent, and the analog for formic acid of the quantity 14 for water.

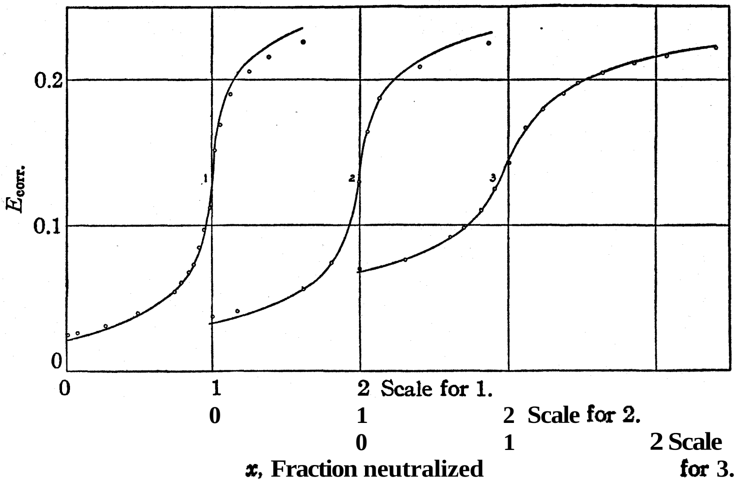

Fig. 2.

Figure 2 presents titration curves 1, 2 and 3 corresponding, respectively, to Tables I, II and III. The plotted points are the experimental values corrected to constant (initial) volume by means of the relationship

$$E_{corr.} = E_{obs.} + 0.0591 \log \frac{V_2}{V_1}$$

where V_2 is the volume corresponding to $E_{obs.}$ at any point during the titration and V_1 is the initial volume. The smooth curves are calculated by the equations

$$E = E_0 - 0.0591 \log [HCO_2']$$

$$X = 1 + \frac{K}{[HCO_2']C} - \frac{[HCO_2']}{C}$$

where X is fraction neutralized, C is the initial concentration of sodium formate, K is obtained from the average pK for the titration concerned, which is given in the tables, and E_0 is chosen by graphical methods to give the best fit. The latter of the above equations is essentially that of Eastman.[11]

Within a titration there is satisfactory agreement in the values of pK and likewise between observed and calculated curves. This would not be the

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

case if there were any great change in liquid junction potential during the titration; it would not be the case if either benzene sulfonic acid or sodium formate were anything but strong electrolytes in this medium; it would not be the case if the activity coefficients of hydrogen ion were subject to large specific effects instead of being determined principally by the total ion concentration. The pK values obtained do therefore give a real measure of the self-ionization of the solvent formic acid.

In the titration of certain apparently strong bases in the solvent acetic acid, Hall and Werner obtained curves which agree with the assumptions here used in the calculation of pK, but their titration curves for weak bases and their dilution curves for both strong and weak bases indicate the presence of very great salt effects accompanying the large changes in total ion concentration which occur in these cases but not in the titration of a strong base. Such intense interionic forces manifested by large salt effects are, however, absent in formic acid. Thus the pK is **5.65** at a salt concentration of **0.13** molar, **5.73** at a salt concentration of **0.075** molar and **5.83 at** a salt concentration of **0.022.** Furthermore, the agreement of these potentiometric values with the figure which may be calculated from the conductivity measurements of Schlesinger and his co-workers is as close as that of the corresponding values for aqueous solutions. They found at 25° a conductivity at infinite dilution for ammonium formate in formic acid of **70.4 r.o.**, for ammonium chloride of **52 r.o.**, and for hydrogen chloride of **75 r.o.**, the latter two values being somewhat uncertain on account of incomplete ionization of the hydrochloric acid and solvolysis of ammonium chloride. The conductivity 6.3×10^{-5} which was found for pure formic acid leads to a pK of 6.3, somewhat larger than our values, as it should be, since it is calculated for zero electrolyte concentration.

The titration data on the acid side of the end-point may be considered as a determination of the effect of varying acid concentration upon the hydrogen-ion activity with a constant concentration of salt present. This excess foreign electrolyte should tend to decrease variations in activity coefficients.[12] These dilution curves for benzene sulfonic acid in the presence of the three different salt concentrations are shown in Fig. 3, which also includes a dilution curve for benzene sulfonic acid without any salt present. The data for the last curve are given in Table IV. Where salt is present the curves are straight lines with the theoretical slope. In the absence of salt the slope is still about 70% of the theoretical value for a strong electrolyte.

From these various considerations it appears that formic acid is **a** solvent in which salt effects are **not** extraordinarily great **as** compared with water: in terms of a physical chemistry of solutions which has been based largely upon the study of aqueous solutions it may be called a normal solvent.

[12] Bronsted and Pedersen, *Z. physik. Chem.*, **103**, 307 (1922).

TABLE IV

DILUTION DATA: 0.4374 MOLAR BENZENE SULFONIC ACID IN THE ABSENCE OF SALT

Acid added to 10.18 cc. of formic acid, cc.	$E_{obs.}$, volt	Log C_a	Add added to 10.18 cc. of formic acid, cc.	$E_{obs.}$, volt	Log C_a
0	0.1515	.....	0.75	0.2206	−1.523
0.07	.1794	−2.524	1.15	.2265	−1.354
.18	.1937	−2.119	1.81	.2318	−1.182
.28	.2033	−1.931	2.80	.2365	−1.027
.45	.2115	−1.733			

Because the ion product constant of formic acid is 10^8 times that of water, the break at the end-point of a titration is considerably less in formic acid than in water, and the range of acids and bases which can be titrated is more limited. A tenth normal solution of a base with an ionization constant less than 3×10^{-5} will give a titration curve with no inflection point.[13]

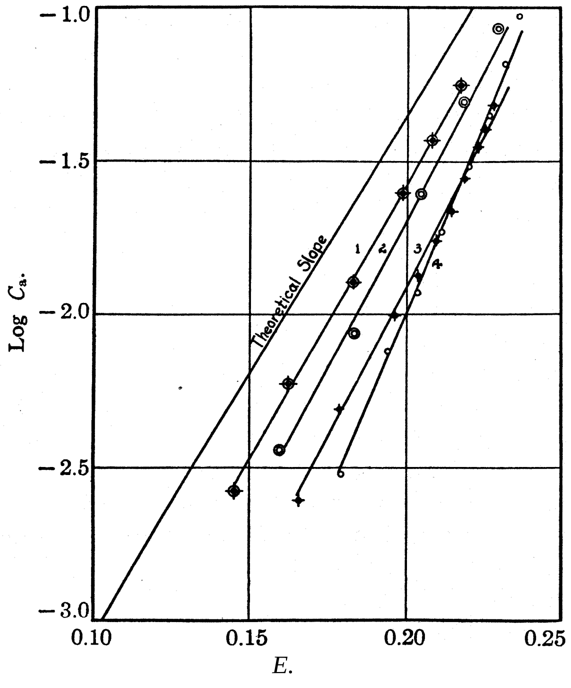

Fig. 3.—Dilution of benzene sulfonic acid Curve 1, data from Table I; Curve 2, data from Table II; Curve 3, data from Table III; Curve 4, data from Table IV.

If free hydrogen ions are incapable of existence in solution, and if ionization of a solvent depends upon its basicity as well as upon its acidity, the decrease in basicity in the transition from water to formic acid must be less than the increase in acidity.

[13] Roller, THIS JOURNAL, 50, 1 (1928).

Other Bases.—The behavior of several other basic substances in formic acid was investigated with the object of acquiring information as to the strengths of such substances in this solvent, and of learning more about the degree of acidity of the solvent itself.

To judge from color, benzene-azo-dimethylaniline and benzene-azo-diphenylamine are completely ionized, not only in formic acid but even in sodium formate–formic acid solutions. In water these indicators are so weakly ionized that their color changes occur at P_H 2.9–4.0 and P_H 1.2–2.1, respectively.[14]

Benzalacetophenone, which is so weak a base in acetic acid that it cannot be titrated,[15] imparts a yellow color to formic acid which is destroyed by the addition of a considerable quantity of sodium formate. This fading is due presumably to the reversal of the ionization

$$\underset{\text{colorless}}{B} + HCO_2H \rightleftharpoons \underset{\text{colored}}{BH^+} + HCO_2^-$$

Triphenylcarbinol is also so weakly basic in acetic acid that it cannot be titrated in that solvent.[7] It likewise gives a yellow solution in formic acid, which is decolorized by excess of sodium formate. Data for its titration with benzene sulfonic acid in formic acid solution are presented in Table V. The constancy of the pK values and their agreement with the values obtained with sodium formate show that it is a univalent strong electrolyte.

TABLE V

TRIPHENYLCARBINOL: BENZENE SULFONIC ACID (p-BENZOQUINHYDRONE ELECTRODES)

0.0002368 mole of triphenylcarbinol used (= 21.51 cc. of 0.01101 molar triphenylcarbinol); 0.4374 = titer of benzene sulfonic acid; 0.541 cc. of benzene sulfonic acid = theoretical end-point.

Acid added, cc.	x = Fraction of base neut.	$E_{obs.}$, volt.	E, volt (corr. to const. vol.)	C_b	pK (referred to C_a = 0.00583)
0	0	0.0951	0.0951	0.01101	5.88
0.112	0.207	.1000	.1002	.00869	5.90
.195	.360	.1053	.1055	.00698	5.91
.264	.487	.1132	.1135	.00557	5.87
.362	.668	.125	.1254	.00358	5.86
.481	.890	.1484	.1490	.00119	5.95[a]
				C_a	pK (referred to C_b = 0.00869)
0.631	1.165	0.1743	0.1750	0.00178	6.07[a]
.839	1.55	.1949	.1959	.00583	5.90
1.121	2.07	.2073	.2087	.01119	5.83
					Average 5.875

[a] Omitted in the average.

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[14] W. Mansfield Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Maryland. 1928, p. 77.

[15] Conant and Hall, THIS JOURNAL, 49, 3062 (1927).

There is evidence however that the ionization of triphenylcarbinol is more complex. Hantzsch[16] found that the freezing point depression which it produces in sulfuric acid indicates the formation of four instead of two products of ionization, probably by the reaction

$$(C_6H_5)_3COH + 2H_2SO_4 \rightleftharpoons (C_6H_5)_3C^+ + OH_3^+ + 2HSO_4^-$$

and Conant and Hall have found evidence that the reaction of the carbinol with strong acids in acetic acid solution produces water.

An ionization of the sort found by Hantzsch would make triphenylcarbinol act like a diacid base. That it acts here like a monoacid base corroborates the conclusion (for which direct evidence is given later) that water has a negligible basicity in formic acid. If the reaction is

$$(C_6H_5)_3COH + HCO_2H \rightleftharpoons (C_6H_5)_3C^+ + HCO_2^- + H_2O$$

the addition of water should decrease the formate-ion concentration and therefore increase the acidity. Using the utmost precautions to exclude water other than known amounts deliberately added, it was found that addition of water up to a concentration of 1% or 0.7 molar to a solution of triphenylcarbinol in formic acid was accompanied by a total increase in potential of only 0.0025 volt. This is an eighty-fold increase over the maximum concentration of water which, it is believed, could have existed in the original solution. The surprisingly small effect found may perhaps arise from a balancing of the above acidity-increasing reaction by a small basic ionization of the water, but some such reaction as

$$(C_6H_5)_3COH + HCO_2H \rightleftharpoons (C_6H_5)_3COH_2^+ + HCO_2^-$$

is also worthy of consideration. This is analogous to the reaction of hydroxo-pentammine cobaltic ion with acids.

Preliminary experiments with urea in formic acid indicated that a slow reaction involving changes in acidity takes place, and precise titrations were impossible. Nevertheless it was clear qualitatively that urea is a strong or moderately strong base in formic acid, Hall and Conant[7] found that urea is a very weak base in acetic acid, and its ionization constant in aqueous solution is only 10^{-14}.

The complete ionization of these bases, which are very weak in water and even in acetic acid, demonstrates the extremely high degree of acidity attainable in formic acid solutions.

If water and ether are bases in the sense that ammonia and the amines are, and there is much evidence to support such a conclusion, they are extremely weak bases, decidedly weaker than are urea and the halochromic ketones and carbinols. For example, 8.0 cc. of a 1.0 molar solution of water in formic acid titrated into 13 cc. of a 0.53 molar solution of benzene sulfonic acid caused a decrease in potential of only 0.025 volt. A large part of this change may be attributed to dilution of the acid alone. Like-

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[16] Hantzsch, *Z. physik. Chem.*, 61, 257 (1907).

wise it was found that a 1.0 molar water solution was approximately 0.015 volt less acid than pure formic acid, Ether is also a very weak base: 7.4 cc. of a 1.0 molar solution of ether in formic acid added to 15 cc. of a 0.5 molar benzene sulfonic acid solution caused a potential change of only 0.026 volt, nearly half of which may be attributed to dilution.

The amounts of water and ether added in these experiments are so large and the changes in potential so small that a change in the nature of the solvent cannot be neglected as a possible source of part or all of the effect. The ionization constants (3×10^{-6} for water and 5×10^{-6} for ether) that may be calculated from these data cannot therefore be given much quantitative validity.

Measured by the ionization of dissolved weak bases, the solvent formic acid is very much more acid than the solvent acetic acid—the ratio of the acidity constants must be more than 10^4. Most of the difference is a medium effect rather than a difference in the inherent acidities of the two acids, for the ionization constant of formic acid in water is only ten times that of acetic acid in the same solvent. This difference in the properties as a medium is exactly what must be expected from the fact that formic acid is a better salt solvent, is a solvent in which interionic forces and therefore ionic activity coefficients are smaller than they are in acetic acid.[2]

Summary

1. Acid–base titrations have been carried out potentiometrically in the solvent formic acid. Benzene sulfonic acid has been found to be a strong acid, and sodium formate, triphenylcarbinol and urea have been found to be strong bases.

2. The ion product constant of the solvent has been calculated with a result in good agreement with that obtained from the conductivity data of Schlesinger. Its large value indicates that formic acid does not differ from water as much in basicity as it does in acidity.

3. Extremely pronounced salt effects were not found to occur in formic acid. In this respect it resembles water more than it does acetic acid.

4. Water and ether were found to have little or no basic properties in this solvent, and their basicities are therefore decidedly smaller than are those of urea and of the halochromic ketones and carbinols.

5. The ratio of the acidity of the solvent formic acid to that of the solvent acetic acid is much greater than the ratio of the acidities of the solutes formic and acetic acids in water. This is interpreted as the result of a medium effect predicted from other known properties of the two solvents.

NEW YORK, N. Y.

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

THE CALCULATION OF FREE ENERGY FROM SPECTROSCOPIC DATA

BY W. F. GIAUQUE

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For many years it has been evident that the utilization of the observed energy levels of atoms and molecules was destined to occupy a prominent place in the application of thermodynamics and statistics to chemistry. However, it is doubtful whether the very real simplicity of this application has been appreciated as it should be. Perhaps this is not surprising when one considers the unnecessarily complicated methods often used in treating such problems. It is the purpose of this paper to give the few simple statements necessary in connection with the exact determination of certain thermodynamic properties from the energy levels of matter as supplied by spectroscopy.

At the present time it is possible to make accurate calculations only for the perfect gaseous state. Interpreted spectroscopic data are available only for relatively simple molecules.

For the usual purposes of chemistry it is convenient to consider a large group of molecules as a single state without investigating the intimate details of their individual existences. However, in order to make a precise statistical calculation of a thermodynamic property, one must have an itemized account of all the states among which the molecules are distributed in appreciable concentrations. It may be well to add that the state of a molecule has a perfectly definite meaning only to the extent to which it is not appreciably influenced by neighboring molecules.

Let us be clear as to the meaning of a state. Every state corresponds to certain definite quantum specifications which are not possessed in every particular by any other state. Fortunately spectroscopy supplies the necessary information about atomic and molecular states and often more accurately than is necessary for ordinary purposes.

Every state is assumed to have equal statistical weight. This means that given equal opportunity to possess the energies necessary for their separate existences, all states are equally probable. The convenient use of *a priori* probability to include a group of states has caused some ambiguity in the use of the term state. A statement to the effect that a certain "state" has an *a priori* weight of three, means that the "state" is really three states which have been grouped together for simplicity of calculation. This is customary when the states have so nearly the same energies that they are affected in nearly the same way by temperature. However, it should be remembered that they are individual states in a statistical sense.

The problem of finding the distribution of atoms and molecules among the various possible states existing in a gas may, for convenience, be divided into two parts, namely, the problem of translation, and that dealing with all other possible energy absorption. The quantum-statistical treatment of the properties of an ideal gas was first given by Sackur[1] and by Tetrode.[2] Later Stern[3] and Ehrenfest and Trkal[4] contributed much clearer treatments. The logic of these earlier treatments left much to be desired, but this difficulty has recently been removed by the introduction of Bose–Einstein statistics. A very satisfactory treatment of this subject, with references to the previous work, has been given by Lewis and Mayer.[5] The final results for the properties of an *ideal* gas possessing translation alone are always the same for the various treatments which have been given. We have nothing to add to this subject but recall attention to the fact that the translational properties of all molecules, however complicated, are represented by the same equations when they are in the ideal gas state. This will be used as a starting point. The equations for the entropy of translation will be quoted later.

The thermodynamic properties of gases are usually referred to the standard state, which is the ideal gas state, and this may be treated simply and accurately when the necessary energy levels are available. The corrections to the actual gas at moderate pressures may usually be neglected at ordinary temperatures or above, but in any case are readily obtained from the data of state. The determination of the distribution of atoms and molecules among the various possible states may be approached by means of thermodynamics or by statistics. The usual thermodynamic method considers the equilibrium between any two states

$$\mathrm{B} = \mathrm{B}' \qquad \Delta F^\circ = -RT \ln \frac{n'}{n}$$

There is no entropy change in such a transition since each of the states has unit a *priori* statistical weight. Thus for this simple process the free energy change $\Delta F = \Delta E$, the energy change, when the particles are taken to be a perfect gas. Then the ratio of the numbers in the two states

$$\frac{n'}{n} = e^{-\Delta E/RT} = e^{-(\epsilon' - \epsilon)/kT} \quad \text{the Boltzmann factor}$$

$\epsilon' - \epsilon$ and k refer to the energy difference and the gas constant per molecule, respectively.

Derivations of the Boltzmann factor from statistics may be found in numerous books dealing with statistical mechanics. A simple derivation has been given by Lewis and Mayer.[5] In agreement with Einstein they show that the Boltzmann factor is not quite correct, due to quantum

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[1] Sackur, Ann. *Physik*, 36,968 (1911).

[2] Tetrode, *ibid.*, 38, 434 (1912).

[3] Stern, *Physik. Z.*, 14, 629 (1913); *Z. Electrochem.*, 25, 66 (1919).

[4] Ehrenfest and Trkal, *Proc. Akad. Sci. Amsterdam*, 23,162 (1920).

[5] Lewis and Mayer, *Proc. Nat. Acad. Sci.*, 15,208 (1929).

degeneracy, but since our discussion will deal only with the standard state which is non-degenerate by definition, we may accept the Boltzmann factor as exactly true.

With the assistance of the Boltzmann factor one may readily obtain the desired thermodynamic properties. Let N be Avogadro's number and A the number of molecules in the lowest energy, or zero state (excluding translation). Then as usual the number in the first state is equal to $Ae^{-\epsilon_1/kT}$, where ϵ_1 is the observed energy per molecule with reference to the zero state. The number in the r^{th} state will be $Ae^{-\epsilon_r/kT}$. From this it follows that

$$N = p_0A + p_1Ae^{-\epsilon_1/kT} + p_2Ae^{-\epsilon_2/kT} + \dots \tag{1}$$

where the p's are the *a priori* probabilities referred to above and it may be well to repeat for emphasis that each term in the above expression is actually p separate terms with so nearly the same Boltzmann factors that the difference may be neglected. The total energy above the zero point of the system (excluding translation) is given by the expression

$$E^\circ - E^\circ_0 = 0p_0A + \epsilon_1p_1Ae^{-\epsilon_1/kT} + \epsilon_2p_2Ae^{-\epsilon_2/kT} + \dots \tag{2}$$

where E°_0 is the energy of the substance in the perfect gas state at the absolute zero of temperature. The superscript ° is used to designate a property of the substance in its standard reference state, in this case the hypothetical ideal gas state with a pressure of one atmosphere. This follows the conventions of Lewis and Randall,[6] which will be used where possible. Eliminating A from Equations 1 and 2, and making use of the abbreviation afforded by the summation sign

$$E^\circ - E^\circ_0 = N\frac{\Sigma\epsilon pe^{-\epsilon/kT}}{Zpe^{-\epsilon/kT}} \tag{3}$$

$$= RT^2\frac{\mathrm{d}\ln Q}{\mathrm{d}T},\ \text{where} \tag{4}$$

$$Q = p_0 + p_1e^{-\epsilon_1/kT} + p_2e^{-\epsilon_2/kT} + \dots \tag{5}$$

These series contain terms for every state that the molecule can assume.

Differentiation of $E^\circ - E^\circ_0$ with respect to T gives the heat capacity due to the degrees of freedom considered, thus

$$\frac{\mathrm{d}E^\circ}{\mathrm{d}T} = \frac{N}{kT^2}\left[\frac{\Sigma\epsilon^2pe^{-\epsilon/kT}}{\Sigma pe^{-\epsilon/kT}} - \left(\frac{\Sigma\epsilon pe^{-\epsilon/kT}}{\Sigma pe^{-\epsilon/kT}}\right)^2\right] \tag{6}$$

$$= -R\frac{\mathrm{d}}{\mathrm{d}T}\frac{\mathrm{d}\ln Q}{\mathrm{d}\,1/T}\,^{7} \tag{7}$$

a well-known equation which was first applied to the actual energy levels of a molecule by Hicks and Mitchell,[8] who, at the suggestion of Tolman, calculated the rotational–vibrational heat capacity of hydrogen

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[6] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923.

[7] Reiche, Ann. *Physik*, 58, 657 (1919).

[8] Hicks and Mitchell, THIS JOURNAL, 48, 1520 (1926).

chloride. Their results are unfortunately marred by an error in connection with the *a priori* probabilities."

Later the heat capacity of hydrogen chloride was correctly calculated by Hutchisson.[10]

The entropy can be calculated very simply from the observed energy levels of molecules by a method to be given below, the principle of which is due to Tolman and Badger,[11] who, assuming rigid molecules, obtained expressions for the rotational entropy. Their paper unfortunately contains a number of errors in connection with the neglect of integration constants due to the multiple *a priori* probabilities of the zero state in several of their assumed cases.

It was shown by Giauque and Wiebe[9] that the equation given by Tolman and Badger holds exactly for molecular entropy due to rotation–vibration or electron excitation, regardless of how irregular these levels might be.

The method is as follows

$$\mathrm{d}S^\circ = \frac{\mathrm{d}E^\circ}{\mathrm{d}T}\cdot \mathrm{d}\ln T \tag{8}$$

$$S^\circ - S^\circ_0 = \int_0^T \frac{\mathrm{d}E^\circ}{\mathrm{d}T}\cdot \mathrm{d}\ln T \tag{9}$$

$$= -R\int_0^T \frac{\mathrm{d}}{\mathrm{d}T}\,\frac{\mathrm{d}\ln Q}{\mathrm{d}\,1/T}\cdot \mathrm{d}\ln T \tag{10}$$

$$= R\left[\ln Q + T\frac{\mathrm{d}\ln Q}{\mathrm{d}T}\right]_0^T \tag{11}$$

$$= R\left[\ln Q_T - \ln Q_0 + T\frac{\mathrm{d}\ln Q_T}{\mathrm{d}T}\right] \tag{12}$$

$$= R\left[\ln \Sigma p e^{-\epsilon/kT} - \ln p_0 + \frac{1}{kT}\,\frac{\Sigma p\epsilon e^{-\epsilon/kT}}{\Sigma p e^{-\epsilon/kT}}\right] \tag{13}$$

Particular attention is called to the term $-R\ln p_0$ in Equation 13 since this has been the cause of considerable misunderstanding. p_0 represents the number of states which have nearly the energy of the zero state and have thus been grouped together for convenience. However, this method leads to an assumed situation where even at the absolute zero of temperature the molecules are distributed equally between p_0 states, thus leading to a zero point entropy of $R\ln p_0$. The question as to whether this could actually happen at the unattainable absolute zero, infinite volume and zero magnetic and electric field strengths which would be necessary under equilibrium conditions need not seriously concern us in this case. $S^\circ_0 = R\ln p_0$ and S°, the absolute entropy, is given by

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[9] Giauque and Wiebe, THIS JOURNAL, 50, 101 (1928).

[10] Hutchisson, *ibid.*, 50, 1895 (1928).

[11] Tolman and Badger, *ibid.*, 45, 2277 (1923). Urey, *ibid.*, 45, 1445 (1923), essentially used this method by graphically integrating one of Reiche's heat capacity equations.

$$S^\circ = R\left[\ln Q_T + T\frac{\mathrm{d}\ln Q}{\mathrm{d}T}\right] \qquad (14)$$

This equation, which holds for all types of states which have been observed, is so general that it should hold for any that are likely to be discovered. This includes the multiplicities due to nuclear effects such as spin.

We believe it is desirable to give another, even simpler, derivation of the important Equation 14, which is the foundation of all the important equilibrium data which may be obtained from spectroscopic observations on molecules.

Let us consider a box with two compartments and a total volume such that it will hold one mole of an ideal gas at pressure P. Let one compartment be filled with gas 1 and the other filled with gas 2, each at pressure P. If the two gases are allowed to intermix uniformly, the entropy increase is given by"-

$$AS^o = -R\,(N_1 \ln N_1 + N_2 \ln N_2) \qquad (15)$$

where N_1 and N_2 refer to the respective mole fractions of the two gases. In general when there are a large number of gases and corresponding compartments in the molal box, the expression for the increase in entropy on mixing becomes

$$AS^o = -R(N_1 \ln N_1 + N_2 \ln N_2 + \ldots N_r \ln N,) \qquad (16)$$

It is extremely useful to regard the various states among which molecules are distributed as supplying the basis for referring to different kinds of molecules in much the same manner as it is convenient to distinguish between optical isomers for some purposes. The number of the molecules in each of the states (excluding translation) is so large that it is convenient to think of a gas having such degrees of freedom as rotation, vibration and electron excitation as consisting of a mixture of a large number of kinds of gases, each kind being distinguished by its quantum numbers.

Let us imagine the molal box to be divided into a sufficient number of compartments of such volumes as are necessary to contain the equilibrium numbers of molecules of each kind or state (excluding translational states), at pressure P. Each of the compartments will contain what may be considered as a perfect monatomic gas. Each molecule within a given compartment is like every other within the same compartment except for the translational distribution. In such a case as that described, the total entropy is simply that of a monatomic gas. The entropy due to all other degrees of freedom in the equilibrium mixture is just the entropy associated with the uniform mixing of the various segregated portions. It may be well to emphasize in connection with the above statements that zero entropy with regard to a certain degree of freedom in no way implies that the molecules are necessarily all in the lowest energy state but only

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[12] Lewis and *Randall*, Ref. *6*, p. *440*.

that all the molecules are in the same state, the "lack of randomness" of Lewis and Gibson.[13]

The entropy of mixing, referred to above, may be calculated as follows

$$N_0 = \frac{1}{Q},\ N_1 = \frac{e^{-\epsilon_1/kT}}{Q},\ \text{etc.} \tag{17}$$

From Equation 16

$$\Delta S^\circ = -R\left[p_0 \times \frac{1}{Q}\ln\frac{1}{Q} + p_1 \times \frac{e^{-\epsilon_1/kT}}{Q}\ln\frac{e^{-\epsilon_1/kT}}{Q} + \ldots\right] \tag{18}$$

$$= R\left[\ln Q + \frac{1}{kT}\frac{\Sigma p\epsilon e^{-\epsilon/kT}}{Q}\right] \tag{19}$$

$$= R\left[\ln Q + T\frac{\mathrm{d}\ln Q}{\mathrm{d}T}\right]$$

which is the previous equation (14). The significance of the p's before the terms in Equation *18* is that there are p terms of equal mole fraction.

The Absolute Entropy.—The well-known equations for the translational entropy of a gas, for which references were given earlier, are

$$S^\circ = \frac{3}{2}R\ln M + \frac{3}{2}R\ln T + R\ln V + \frac{5}{2}R + C \tag{20}$$

where M is the molecular weight, V the molal volume in cc. and $C = R \ln [(2\pi k)^{3/2}/h^3N^{5/2}] = -16.024$ calories per mole per degree,[14] where h is Planck's constant, and from the gas law

$$S^\circ = \frac{3}{2}R\ln M + \frac{5}{2}R\ln T - R\ln P + \frac{5}{2}R + C + R\ln R \tag{21}$$

when P is the pressure in atmospheres. $C + R \ln R = -7.267$.

To obtain the absolute entropy the amount $R \ln Q + RT(\mathrm{d}\ln Q/\mathrm{d}T)$ must be added to either Equation *20* or *21*.

The Calculation of Free Energy.—The free energy F is given by the equation[6]

$$F = H - TS \tag{22}$$

where the heat content

$$H = E + PV \tag{23}$$

For the ideal gas

$$H^\circ = E^\circ + RT \tag{24}$$

Then

$$F^\circ = E^\circ + RT - \frac{3}{2}RT\ln M - \frac{5}{2}RT\ln T + RT\ln P - \frac{5}{2}RT - CT - RT\ln R - RT\ln Q - RT^2\frac{\mathrm{d}\ln Q}{\mathrm{d}T} \tag{25}$$

The total energy E° is equal to the sum of the energy at the absolute zero E_0°, the energy of translation *3/2* RT, and the energy due to all other degrees of freedom $RT^2(\mathrm{d}\ln Q/\mathrm{d}T)$.

$$E^\circ = E_0^\circ + \frac{3}{2}RT + RT^2\frac{\mathrm{d}\ln Q}{\mathrm{d}T} \tag{26}$$

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[13] Lewis and Gibson, **Ref.** 6, Chap. XXXI.

[14] **The** values used for all natural constants are those given by "International Critical Tables." Vol. I, p. 16.

Combining Equations 25 and 26

$$F^\circ - E_0^\circ = -\frac{3}{2}RT\ln M - \frac{5}{2}RT\ln T + RT\ln P - CT - RT\ln R - RT\ln Q \quad (27)$$

When the necessary atomic or molecular energy levels are known, Q may be calculated for any desired temperatures and tables of $F^\circ - E_0^\circ$, or preferably $(F^\circ - E_0^\circ)/T$ may be prepared. By combination of these values for the various substances involved in a given reaction, the value of $\Delta(F^\circ - E_0^\circ)$ may be obtained. F° is the nomenclature of Lewis and Randall for the standard state, in this case, the hypothetical ideal gas state with $P = 1$ atmos.

$$\Delta F^\circ = -RT\ln K^6 = \Delta(F^\circ - E_0^\circ) + \Delta E_0^\circ \quad (28)$$

From Equation 28 the equilibrium constant may be calculated for any desired temperature provided that ΔE_0° may be determined.

The Determination of ΔE_0°.—There are three general methods of evaluating ΔE_0°. (I) When the various excited states of a molecule are known up to dissociation into atoms, ΔE_0° is known for that reaction from spectroscopic data alone. By proper combinations ΔE_0° can then be obtained for other reactions. This method which gives great promise has already been applied to the dissociation of a number of diatomic molecules,[15] while most existing calculations of this type are uncertain, due principally to considerable extrapolation, it seems certain that this difficulty will be minimized by future work on this relatively new method. In several cases where the extrapolation is small, the method already provides our best source of this information.

(II) ΔE_0° may be calculated by means of Equation 28, when one reliable value of the equilibrium constant is known, or if K is known over a range of temperatures, a more reliable value of ΔE_0° may be obtained by making use of the several data.

(III) when ΔH° is known from a calorimetric determination at temperature T, ΔE_0° may be obtained with the assistance of Equations 24 and 26.

$$\text{Thus } \Delta E_0^\circ = \Delta H^\circ - \Delta\left[\frac{5}{2}RT + RT^2\frac{d\ln Q}{dT}\right] \quad (29)$$

Equilibrium between Solids, Liquids and Gases.—There are many cases where it will be necessary to consider equilibrium between some condensed state or states and gases, for example

$$C + \tfrac{1}{2}O_2 = CO$$

Here the third law of thermodynamics may be used for carbon in combination with spectroscopic observations on the gases. Thus

$$F^\circ - E_0^\circ = \int_0^T C_p\,dT - T\int_0^T C_p\,d\ln T \quad (30)$$

Recent values of this function are given by Rodebush and Rodebush.[16]

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[15] Birge, "International Critical Tables," 1929, Vol. V, p. 418.

[16] Rodebush and Rodebush, "International Critical Tables," Vol. V, p. 87.

The F used in these tables is our $F^\circ - E_0^\circ$. These may be combined with the values of $F^\circ - E_0^\circ$ obtained for gases.

It is evident that the $F^\circ - E_0^\circ$ values for gases are of great utility even when no low temperature heat capacity measurements are available. However, as usual, this will necessitate the evaluation of at least one undetermined constant from equilibrium data.

In concluding these derivations, it is interesting to note that the exact determination of $F^\circ - E_0^\circ$ from spectroscopic data is a relatively easy calculation, involving only the summation of the Q series. The calculation of entropy or energy involves, in addition, the temperature derivative of the Q series, in which case the terms do not become negligible so rapidly.

The calculation of heat capacity involves the second derivative of the Q series, which is somewhat more laborious to sum. Fortunately the heat capacity need not be calculated in the process of determining an equilibrium and in many cases the entropy and energy may also be left undetermined.

The calculation of values of the free energy function to high temperatures is now in progress for the atoms and molecules for which the energy levels are known and it is expected that it will be possible to begin publication of this material in the near future.

Summary

Methods and equations for the *exact* calculation of free energy and other properties of the thermodynamic standard state of gases have been discussed.

A simple method of deriving a general expression for the absolute entropy of ideal gases has been given. This covers molecular rotation, vibration, electronic excitation and nuclear spin. In addition the method supplies a valuable insight into the simple relationship of complicated molecular states to the entropy.

The equations given will serve as the basis for an extended series of tabulations of free energy of gases based on available spectroscopic data.

BERKELEY, CALIFORNIA

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

THE ENTROPY OF HYDROGEN AND THE THIRD LAW OF THERMODYNAMICS
THE FREE ENERGY AND DISSOCIATION OF HYDROGEN

BY W. F. GIAUQUE

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The band spectrum data of the hydrogen molecule have recently been considered by Birge, Hyman and Jeppesen.[1] They have shown that the observed rotational energies associated with the vibrational levels may be represented with a very high degree of accuracy by means of simple equations for which they give the constants. Accepting their representation of the observed behavior of the molecule, we will illustrate the application of such data in the exact calculation of several thermodynamic properties. The equations required for this purpose have been given in the preceding paper.[2] These eliminate the necessity of such assumptions as molecular rigidity and other approximations.

These calculations will serve not only in making available important and very accurate thermodynamic properties of the hydrogen molecule, but will furnish an introduction to an extended series of papers in which similar data will be given for the elements and simpler molecules. At the present time calculations have been made on about one-third of the elements and a number of other substances.

A second purpose of this paper is to clear up the numerous misunderstandings which have arisen concerning the effect of nuclear spin on the entropy of hydrogen and the use of this entropy in conjunction with the entropies obtained from the third law of thermodynamics.

The situation existing in hydrogen has been correctly stated in the paper of Giauque and Johnston[3] and the use of the entropy of hydrogen in connection with the third law has been discussed by Kelley[4] as a personal communication from this author. Following this, a paper by Rodebush[5]

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[1] (a) Personal Communication; (b) Hyman and Jeppesen, *Nature,* (March, 1930); (c) Birge and Jeppesen, *ibid.,* (March, 1930).

[2] Giauque, THIS JOURNAL, 52, 4808 (1930).

[3] Giauque and Johnston, *ibid.,* 50, 3221 (1928). Also see Fowler, *Proc. Roy. Soc.,* (London), **118A,** 52 (1928). Fowler's treatment led to an incorrect result.

[4] (a) Kelley, *Ind. Eng.* Chem., 21, 353 (1929); THIS JOURNAL, 51, 1145 (1929).

[5] Rodebush, *Proc. Nat. Acad. Sci.,* 15, 678 (1929). A paper [*Phys.* Rev., 36, 1398 (1930)] has recently appeared in which D. MacGillavry, who did not know of the paper by Rodebush, has raised the same objection, although he agrees with our result. This objection, which concerns the reliability of an *a priori* calculation of the entropy of a system when molecules such as ortho and para hydrogen are not in complete equilibrium, has been answered more specifically by Giauque and Johnston [*Phys. Rw.,* 36, Nov. *15.* (1930)].

We add here for the sake of completeness that most, if not all, of the systems has criticized not only our method of considering the problem, but also the numerical result, although his value is identical with ours. However, confusion has arisen since the paper by Rodebush, while giving the correct value for the absolute entropy of hydrogen, leaves the impression that this value should be used in conjunction with values obtained far other substances from the $\int_0^T C_p \, d \ln T$ with the assistance of the usual extrapolation methods at very low temperatures. The papers of Giauque and Johnston and of Kelley make a very specific point of the fact that this cannot be done. We have learned from a number of personal communications and also from criticism of Kelley for using our correct values, which we have recently noticed, that it is desirable to restate this problem which has implications relating not alone to hydrogen, but to all the elements excepting a few which are without nuclear spin. We will return to this problem later in this paper.

The results of Birge, Hyman and Jeppesen for the normal electronic state of the hydrogen molecule may be represented by the equation

$$E = E_v + B_v m^2 + D_v m^4 + F_v m^6$$

where m has the values $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots\ldots\ldots;\ m = j + \frac{1}{2}$ where j represents the number of units of rotational momentum; v refers to the number of units of vibration in addition to the half unit of zero point vibration. The values of the constants of the above equation are given in Table I.

TABLE I

CONSTANTS IN THE ENERGY EQUATION OF THE HYDROGEN MOLECULE IN CM.$^{-1}$

v	E_v	B_v	v	E_v	B_v
0	0	59.354	7	24281	39.209
1	4161 96	56.404	8	26823	36.121
2	8083	53.630	9	29117	32.930
3	11778.5	50.834	10	31148	29.53
4	15247.5	48 008	11	32883	25.7
5	18489	45 138	$D_v = -0.0465 + 0.00135(v + \frac{1}{2})$		
6	21501	42 210	$F_v = 5.18 \times 10^{-5}$		

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considered by means of thermodynamics or statistics are not in complete equilibrium. Not only "stable" molecules but even the elements are potentially unstable with respect to others.

If we knew the absolute entropies of two organic isomers we believe that no criticism would be made if the total entropy of a system consisting of an isomeric mixture was calculated by adding the entropy of mixing to that of the pure constituents. However, when this generally accepted method is applied to the identical case of the recently discovered hydrogen isomers, the method is considered not plausible.

The calculation of absolute entropy is not appreciably complicated by the co-existence of some non-equilibrium states. The substitution of a lengthy calculation along a reversible path through limiting high temperatures for the simple and direct isothermal reversible path, usually used in such cases, does not increase the certainty of the result. In most cases the former method would require information not yet available.

The conclusion of Heisenberg,[6] on the basis of wave mechanics, that two general classes of hydrogen molecules exist has been amply substantiated by experiment. In the normal electronic state the para form, which has the nuclear spins opposed in the molecule can have only the even molecular rotational levels, $j = 0, 2, 4, 6, \ldots\ldots\ldots$, or $m = \frac{1}{2}, \frac{5}{2}, \frac{9}{2}, \frac{13}{2} \ldots\ldots\ldots$, while the ortho form can have only the odd rotational levels. The ortho hydrogen has three times the statistical weight which it would have in the absence of nuclear spin since the additive coupling of the two half-unit nuclear spins leads to $j_s = 1$ and an *a priori* probability $p_s = 2j_s + 1 = 3$. The para hydrogen with the canceling coupling has $j_s = 0$, $p_s = 2j_s + 1 = 1$. Thus at high temperatures a ratio of 1:3 between para and ortho states is found. The first definite experimental evidence for this ratio was given by Hori[7] from his measurements on the relative intensities of the lines in the band spectrum of hydrogen. Dennison[8] then showed that the long unexplained shape of the rotational heat capacity curve, first obtained experimentally by Eucken,[9] was in complete agreement with the above conditions. It was assumed that the rate of conversion of ortho and para hydrogen into each other is so slow as to be negligible under the conditions of experiment. At the suggestion of E. U. Condon, Giauque and Johnston[3] kept hydrogen at the temperature of liquid air to study the rate of conversion. A bomb containing about 10 moles of hydrogen at a pressure of 75 atmospheres was kept at about 85°K. for 197 days. On liquefying some of this hydrogen the vapor pressure when solid and liquid phases were present was found to have been lowered. Smits[10] has called attention to the fact that ordinary hydrogen has no triple "point" since the solid is in reality a solid solution.

The observed lowering of the vapor pressure, while small, was beyond the limit of experimental error and thus indicated the predicted readjustment of the relative proportions of ortho and para hydrogen. The further experiments promised by these authors were discontinued following the publication of the excellent work of Bonhoeffer and Harteck,[11] who carried out further investigations of the vapor pressure and made quantitative measurements of the rate of conversion with the assistance of a charcoal catalyst and an analytical method depending on the different thermal conductivities of the ortho and para forms. MacLennan and MacLeod[12]

[6] Heisenberg, *Z. Physik*, 41, 239 (1927).

[7] Hori, *ibid.*, 44, 834 (1927).

[8] Dennison, *Proc. Roy. Soc.* (London), 115A, 483 (1927).

[9] (a) Eucken, *Sitzb. preuss. Akad. Wiss.*, 144 (1912); (b) *Ber. deut. physik. Ges.*, 18, 4 (1916).

[10] Smits, *Koninklijke Akad. Wetenschappen Amsterdam*, 32, 603 (1929).

[11] (a) Bonhoeffer and Harteck, *Sitzb. preuss. Akad. Wiss.*, 103 (1929); *(b) Naturwiss.*, 17, 182,321 (1929); (c) Z. *physik. Chem.*, *4B*, 113 (1929).

[12] McLennan and MacLeod, *Nature*, 113, 152 (1929).

have shown from measurements of Raman spectra on liquid hydrogen that the two forms exist under this condition. Further substantiation from heat capacity and heat content measurements will be considered later.

The Equilibrium Composition of Hydrogen.—From Equation 1 of the previous paper

$$N = p_0A + p_1Ae^{-\epsilon_1/kT} + p_2Ae^{-\epsilon_2/kT} + \dots\dots = AQ$$

where N is Avogadro's number and A the number of molecules in the lowest energy state, we have calculated the ratio of ortho and para molecules existing at various temperatures under equilibrium conditions. In place of the usual rotational *a priori* weights 1, 3, 5, 7, 9, ..., the weights 1, 9, 5, 21, 9, ..., must be used.

The fraction of the molecules in the para states is given by

$$\frac{p_0 + p_2e^{-\epsilon_2/kT} + p_4e^{-\epsilon_4/kT} + \dots\dots}{p_0 + p_1e^{-\epsilon_1/kT} + p_2e^{-\epsilon_2/kT} + p_3e^{-\epsilon_3/kT} \dots\dots} = \frac{Q_{\text{para}}}{Q}$$

The energies used in calculating the exponents are the actual energy levels of the molecule and, of course, include such effects as work done in the stretching of the molecule with increasing rotation and the change in the moment of inertia due to the same cause. The results are given in Table II.

TABLE II

EQUILIBRIUM DISTRIBUTION OF HYDROGEN MOLECULES IN ORTHO AND PARA ROTATION STATES

T, degrees absolute	Percentage para	T, degrees absolute	Percentage para	T, degrees absolute	Percentage para
0	100	75	51.776	250	25.257
15	99.989	100	38.461	273.1	25.141
20	99.814	125	31.871	298.1	25.074
25	98.996	150	28.544		
30	96.951	175	26.836		
40	88.547	200	25.953		
50	76.798	225	25.495		

It will be seen that the 1:3 ratio is closely approximated at room temperature

The Energy Content of Hydrogen.—From Equations 1 and 2 of the previous paper the total energy of the system (excluding translation) with reference to the zero state may be calculated.

$$E^\circ - E^\circ_0 = \frac{N\Sigma p\epsilon e^{-\epsilon/kT}}{\Sigma pe^{-\epsilon/kT}}$$

The calculations have been made for four conditions, pure para hydrogen, pure ortho hydrogen, for the equilibrium mixture of the two, and for the 1:3 mixture. The first, third and fourth cases are easily realizable experimentally, while the data on ortho hydrogen are useful for the calculation of the wide range of realizable systems intermediate between pure para hydrogen and the equilibrium mixture. The values are given in Table

III. The amount $3/2RT = 2.9804$ T cal./deg. per mole should be added for translational energy if the total energy is required.

TABLE III

ENERGY OF HYDROGEN GAS WITH REFERENCE TO THE ZERO STATE

(Translational Energy is not Included)

T, degrees absolute	Calories per mole Pure para hydrogen	Pure ortho hydrogen	Equilibrium mixture	$^1/_4$ Para $^3/_4$ Ortho
0	0.00	337.17	0.00	252.88
15	.00	337.17	.04	252.88
20	.00	337.17	.63	252.88
25	.00	337.17	3.39	252.88
30	.00	337.17	10.28	252.88
40	.05	337.17	38.63	252.89
50	.20	337.18	78.38	252.94
75	5.77	337.22	165.61	254.36
100	30.56	338.59	219.78	262.17
125	80.09	341.83	258.41	276.39
150	146.61	351.40	292.94	300.20
175	219.09	368.54	328.44	331.17
200	290.22	393.59	366.76	367.75
225	357.04	425.69	408 19	408.53
250	419.27	463.46	452.30	452.41
273.1	473 34	502.16	494.84	494.91
298.1	529.12	546.92	542.46	542.47

Elbe and Simon[13] have calorimetrically determined the difference in energy content of the 1:3 mixture and the equilibrium state by means of adsorption of each on charcoal. At 77.5°K. the difference found was 74 calories per mole. By interpolation we find the value of 83 calories per mole at this temperature. At 20 4°K. the difference was 241 calories against 252 calories from Table III. Considering the difficulty of experiment, this is good agreement and is well within the limits of error indicated by Elbe and Simon, who made a similar comparison.

The Heat Capacity of Hydrogen.—The heat capacity for several conditions of hydrogen was calculated from Equation 6 of the previous paper.

$$\frac{dE^\circ}{dT} = \frac{N}{kT^2}\left[\frac{\Sigma\epsilon^2pe^{-\epsilon/kT}}{\Sigma pe^{-\epsilon/kT}} - \left(\frac{\Sigma\epsilon pe^{-\epsilon/kT}}{\Sigma pe^{-\epsilon/kT}}\right)^2\right]$$

For example, in making this calculation for pure para hydrogen, only the even terms are considered in the summations. The method of using the actual energy levels of the molecules gives the heat capacity with an accuracy exceeding that of any direct experimental measurement. The values are given in Table IV. The value of 3/2 R = 2.9804 cal./deg. per mole should be added to these values on account of translation if the total heat capacity at constant volume is required.

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[13] Elbe and Simon. *Z. physik. Chem*., **6B**, 79 (1929).

TABLE IV

HEAT CAPACITY OF HYDROGEN GAS (EXCLUDING TRANSLATION)

Calories per degrees per mole

T, degrees absolute	Pure para hydrogen	Pure ortho hydrogen	Equilibrium mixture	$^1/_4$ Para $^3/_4$ Ortho
0	0.0000	0.0000	0.0000	0.0000
15	.0000	.0000	.0028	.0000
20	.0000	.0000	.2649	.0000
25	.0000	.0000	.9196	.0000
30	.0001	.0000	1.8795	.0000
40	.0049	.0000	3.4465	.0012
50	.0399	.0000	4.1042	.0100
75	.5177	.0079	2.7263	.1353
100	1.5041	.0731	1.7498	.4309
125	2.3981	.3131	1.4138	.8343
150	2.8451	.5271	1.3801	1.1066
175	2.9046	.8464	1.4708	1.3610
200	2.7674	1.1512	1.5965	1.5553
225	2.5777	1.3023	1.7148	1.6211
250	2.4056	1.6049	1.8101	1.8051
273.1	2.2819	1.7378	1.8756	1.8738
298.1	2.1862	1.8377	1.9254	1.9248

Similar calculations were given by Dennison[8] and by Beutler[14] both of whom assumed the molecule to be rigid. Their results are expressed in terms of the variable B/kT, where B is the same as in the first term of the equation used above to represent the energy levels of the molecule. This can be done only when the condition of rigidity is imposed. By interpolation of Dennison's values it is found that the neglect of molecular stretching leads to results about 1% too low at 200°K. and about 1.3% too low at 298.1°K. The necessity of considering molecular stretching in this connection was pointed out by Kemble and Van Vleck.[15]

The various experimental measurements on the rotational heat capacity of hydrogen have been summarized by Eucken and Hiller,[16] who have carried out a very interesting series of experiments on hydrogen with 95, 43.1, 36.4 and 31.1%, respectively, of the para variety in addition to ordinary hydrogen with 25%. It is interesting to note that when we consider the effect of molecular stretching, the good agreement of the results of Cornish and Eastman[17] with the theoretical curve is further improved.

The Entropy of Hydrogen.—The important and much misunderstood value of the entropy of hydrogen may be calculated from Equation 14 of the previous paper.

$$S^\circ = R\left[\ln \Sigma p e^{-\epsilon/kT} + \frac{1}{kT}\,\frac{\Sigma p\epsilon e^{-\epsilon/kT}}{\Sigma p e^{-\epsilon/kT}}\right]$$

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[14] Beutler, *Z. Physik.* 50, 581 (1928).

[15] Kemble and Van Vleck, *Phys. Rev.*, 21,653 (1923).

[16] Eucken and Hiller, *Z. physik. Chem.*, 4B, 142 (1929).

[17] Cornish and Eastman, THIS JOURNAL, 50,627 (1928).

$$= 4.5750 \left[\log 7.7533 + \frac{3.0839}{7.7533}\right] = 5.889 \text{ E.U.}$$

when $T = 298.1°K$. To this must be added the entropy due to translation, namely 28.090 E.U. This is obtained from the Sackur equation given as Equations 20 and 21 in the previous paper.

$$S° \text{ Translation} = 3/2\ R \ln M + 5/2\ R \ln T - 7.267$$

where M is the molecular weight and the pressure of the gas is one atmosphere.

The absolute entropy of hydrogen is thus found to be **33.98** calories per degree per mole, in agreement with our previous value mentioned above. However, we hasten to add that this is not the value which should be used as the entropy of hydrogen in combination with $\int C_p \text{ d In T}$ for other substances.

This can perhaps best be made clear by discussing the application of the third law of thermodynamics to hydrogen. It was shown by Giauque and Johnston[3] that ordinary solid hydrogen had an entropy of **4.39** E.U. above the vibrational entropy. This is due to the existence of ten kinds of molecules within the solid state. These kinds of molecules are distinguished only in that each has a different rotational or nuclear spin quantum specification. Of these one-fourth are para hydrogen with $j = 0$ and three-fourths are equally divided between nine kinds of ortho hydrogen, with $j_{\text{rot.}} = 1$ and $j_s = 1$, each of the latter therefore making up one-twelfth of the total amount. This can be considered by the usual expression for the entropy of mixing

$$\text{AS} = -1/4 \text{ R} \ln 1/4 - 9/12 \text{ R} \ln 1/12 = 4.39 \text{ E.U.}$$

The best determinations of the heat capacity of condensed hydrogen are due to Simon and Lange,[18] who also directly determined the heat of vaporization. They found that their results on solid hydrogen could be represented by a Debye function with an $h\nu/k = 91$. The most accurate determinations of the heat capacity of hydrogen gas are those of Cornish and Eastman,[17] who used the velocity of sound method at low temperatures. The greatest uncertainty in calculating entropy from the experimental measurements lies in the estimation of the correction of the actual hydrogen gas to the ideal gas at low temperatures, since the heat capacity of the actual hydrogen gas has not been measured at the temperatures of condensed hydrogen. For this reason we have used the heat of vaporization at the melting "point(?)" of hydrogen but even here where the pressure is but **5.38** cm., the correction obtained by combining the thermodynamic equation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$ with the equation of Berthelot is **0.13** E.U., while that obtained from the equation of van der Waals is **0.03** E.U. A summary of the calculation is given in Table V.

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[18] Simon and Lange, *Z. Physik*, **15**, 312 (1923).

TABLE V

CALCULATION OF THE ENTROPY OF HYDROGEN

Solid	Cal./deg. per mole
0–13.95°K., $h\nu/k = 91$	0.52
Fusion, 28.0/13.95	2.01
Vaporization at 5.38 cm. pressure, 217.8/13.95	15.61
Correction to ideal gas	0.13 Berthdot, or .03 van der Waals
Compression from 5.38 cm. to 76.0 cm.	–5.26
$\int_{13.95}^{298.1} C_p \, d \ln T$	16.73
	29.74 Berthelot gas, or 29.64 van der Waals gas

Subtracting the entropy of mixing referred to above from the absolute entropy, the value **33.98 – 4.39 = 29.59 E.U.** is found to be in excellent agreement with the observed value. This is a very interesting confirmation, not only of the truth of the third law, but also of the correctness of the situation assumed to exist in solid hydrogen.

Recently Simon, Mendelssohn and Ruhemann[19] have published a preliminary report of an investigation of the heat capacity of solid hydrogen at the temperatures of liquid helium. They have found that the heat capacity fails to follow the Debye curve and at about 2°K. is increasing with decreasing temperature. For the ordinary mixture this additional loss of entropy amounts roughly to 0.7 E.U. to 2°K. and shows that hydrogen is beginning to dispose of the **4.39 E.U.** referred to above.

In a recent paper Pauling[20] gives convincing reasons for believing that not only hydrogen but many other molecules containing hydrogen are rotating in the solid state. Pauling supports the conclusions of Giauque and Johnston and predicts that the process of losing the **4.39** E.U. will not approximate completion until temperatures below 0.001°K. are reached.

From the above results it will be evident that it is not practical to obtain the absolute entropy of hydrogen from heat capacity measurements alone. It is equally certain that in the case of other substances with nuclear spin, and this includes nearly all substances, heat capacity measurements over the attainable temperature range will not suffice to give the absolute entropy. This situation which would at first sight seem fatal to the exact practical application of the third law of thermodynamics is by no means so serious since there is reason for believing that hydrogen may be the only substance which does not cause a very simple type of deviation for which a correction may be applied.

To make this clear we will consider an important observation of Gibson

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[19] Simon, Mendelssohn and Ruhemann, *Naturwiss.*, 18, 34 (1930).

[20] (a) Pauling, *Phys. Rev.*, 36,430 (1930); (b) Personal communication.

and Heitler,[21a] who carried out, from spectroscopic data, the calculation of the dissociation of gaseous iodine into its atoms. They show with the assistance of wave mechanics that in reactions involving diatomic and monatomic substances that nuclear spin contributes equally to the absolute entropy of the reactants and to the products. Using this fact Gibson and Heitler were able to make a very accurate calculation of the dissociation constant even though the nuclear spin of the iodine atom is unknown. Gibson[21b] has expressed the opinion that cancellation will occur in reactions involving polyatomic molecules.

However, it must be pointed out that the nuclear spin cancellation is only a limiting approximation which is valid when the temperature is high enough. For gas reactions there is little reason for doubting that room temperature is always sufficient. As an example the equilibrium reaction $H_2 = 2H$ would approximate an error of $2 R \ln 2 = 2.75$ E.U. at 20°K. where, at equilibrium, nearly all of the diatomic hydrogen would be in the zero state of the para form which has unit weight, whereas the monatomic hydrogen still retains equal distribution among its spin multiplets. At 100°K. the discrepancy has been reduced to 0.88 E.U., while at room temperature it is negligible. It may also be added that hydrogen shows this effect to a much greater degree than is possible in any other diatomic molecule at the same temperatures and almost certainly to a greater degree than will be found possible in polyatomic molecules. If solid substances always retain the high temperature multiplicity due to nuclear spin over the experimental range used in connection with the third law of thermodynamics, it is obvious that it will be unnecessary to consider it. Very probably this is nearly always true, the one known exception being hydrogen, with some compounds containing hydrogen being somewhat uncertain.

On the experimental side the results of Giauque and Wiebe[22] on hydrogen chloride, hydrogen bromide and hydrogen iodide all prove that the limiting entropy due to spin persists to temperatures below 15°K. They showed that the entropy given by the third law agreed with that obtained from spectroscopic data when nuclear spin was ignored in the calculation. This author will soon publish a paper showing that the available data on iodine lead to the same result. This is particularly important since, in distinction from the polar hydrogen halides, the symmetry of the iodine molecule must lead, as in all such cases, to ortho and para molecular species. Pauling, in the paper referred to above, indicates that this is due to the fact that a molecule like iodine cannot rotate in the solid state, whereas

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[21] (a) Gibson and Heitler, Z. *Physik*, 49, 465 (1928); (b) Gibson, personal communication.

[22] (a) Giauque and Wiebe, THIS JOURNAL, 50, 101 (1928); (b) 50, 2193 (1928); (c) 51, 1441 (1929).

hydrogen can. Experimental work on nitrogen and methane is in progress in this Laboratory in order to decide this question.

From the above it is concluded that all polar molecules which do not have the possibility of ortho and para rotational series of the type illustrated by hydrogen, will retain their high temperature nuclear spin entropy to temperatures far below 1°K. In the case of molecules having two or more similar atoms symmetrically placed within the molecule, all those containing such symmetrically placed atoms other than hydrogen will probably retain their limiting spin entropy to temperatures below 1°K. In the case of hydrogen it must be considered that the size of the proton places it in a class far removed from the other atoms whose "size" depends on the electron configuration about them. Many organic compounds undoubtedly have symmetrically placed hydrogen atoms. This does not necessarily mean that nuclear spin cancellation does not occur, since these molecules differ from hydrogen in that they condense at temperatures where the high temperature nuclear spin entropy is established, whereas the hydrogen molecules are frozen out at temperatures greatly below this point.

In many recent references to the use of the third law in connection with reactions involving hydrogen, the authors seem to feel that the entropy of hydrogen is in doubt. We hope it has been made clear that the entropy of hydrogen is definitely established and that the remaining doubt concerns other molecules which contain hydrogen. Since the effects discussed are of primary importance in connection with the use of the third law of thermodynamics in organic chemistry, it is interesting to note that the predominant isotopes carbon **12** and oxygen **16** are without nuclear spin.

The value of the entropy of hydrogen which should be used in conjunction with data obtained from the third law of thermodynamics is **31.23** E.U. This is the value which has been used by Kelley[4] at our suggestion. It is obtained by subtracting the high temperature nuclear spin entropy $R \ln 4 = 2.75$ **E. U.** from the absolute entropy of hydrogen $33.98 - 2.75 = 31.23$ **E. U.** This places hydrogen on the same basis as other molecules in most of which, and perhaps in all of which, the subtraction is taken care of by the fact that heat capacities are not usually measured below temperatures of a few degrees absolute.

The Dissociation **of** Hydrogen.—Langmuir and Mackay[23] have determined the heat of dissociation of hydrogen and the equilibrium constant over a range of temperatures. They utilized measurements of the energy conducted away from a heated filament operating in hydrogen gas at various pressures. As is well known, the evaluation of the heat of reaction

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[23] (a) **Langmuir,** THIS JOURNAL, 34, 860, 1310 (1912); (b) 37, 417 (1915); (c) **Langmuir and Mackay,** *ibid.*, 36, 1708 (1814).

and dissociation constant from data where both occur as unknowns is very difficult and for this reason no very high accuracy has been claimed for the values obtained. However, with the assistance of the data and methods discussed above it is possible to show that the values of the dissociation of hydrogen given by Langmuir over the temperature range where his method was considered to be reliable are very satisfactory even though their temperature coefficient is somewhat in error.

From Equation 27 of the previous paper we have

$$\frac{F^\circ - E_0^\circ}{T} = -3/2\,R \ln M - 5/2\,R \ln T + R \ln P - R \ln Q + 7.267$$

R = 1.9869 calories per degree per mole.

From the energy equations of Birge, Hyman and Jeppesen[1] the values of the absolute $Q = \Sigma p e^{-\epsilon/kT}$ for the hydrogen molecule have been calculated. The values of $(F^\circ - E_0^\circ)/T$ are given in Table VI.

TABLE VI

ABSOLUTE $(F^\circ - E_0^\circ)/F$ FOR THE HYDROGEN MOLECULE

T	$-\frac{F^\circ - E_0^\circ}{T}$	T	$-\frac{F^\circ - E_0^\circ}{T}$	T	$-\frac{F^\circ - E_0^\circ}{T}$
298.1	**27.191**	1250	**37.069**	3200	44.018
300	**27.235**	1300	37.344	3300	44.259
350	28.285	1400	37.868	3400	44.493
400	**29.193**	1500	**38.360**	3500	44.720
450	29.999	1600	38.825	3600	44.941
500	**30.720**	1700	39.264	3700	45.157
550	31.374	1800	39.678	3800	45.368
600	31.973	1900	40.069	3900	45.574
650	32.524	2000	**40.440**	4000	**45.776**
700	33.035	2100	40.795	4100	45.973
750	**33.512**	2200	41.137	4200	46.166
800	33.959	2300	41.468	4300	46.355
850	34.379	2400	41.789	4400	46.540
900	34.775	2500	**42.100**	4500	46.721
950	35.150	2600	42.402	4600	46.899
1000	**35.507**	2700	42.694	4700	47.074
1050	35.847	2800	42.977	4800	47.246
1100	36.172	2900	43.250	4900	47.416
1150	36.483	3000	**43.514**	5000	**47.584**
1200	36.782	3100	43.770		

The values given in heavy type have been directly calculated, the others have been carefully interpolated.

In calculating the values in Table VI the effect of nuclear spin has been included. However, if these values are to be combined with similar data for substances where the nuclear spin is unknown, and thus is conveniently ignored, the amount of $R \ln 4 = 2.755$ should be added to $(F^\circ - E_0^\circ)/T$. For example, the value of $-(F^\circ - E_0^\circ)/T$ for 298.1°K. becomes 24.436 calories per degree per mole.

For monatomic hydrogen the absolute $Q = 1$ per atom, a multiplicity of 2 arising from nuclear spin with an additional factor of 2 due to the electron spin in this atom. Thus the absolute

$$\frac{F^o - E_0^\circ}{T} = -3/2\,R \ln 1.0076 - 5/2\,R \ln T - R \ln 4 + 7.267$$

In Table VII the values of $+5/2\,R \ln T - 7.267$ are given instead of the whole function because these values are necessary in connection with all other gaseous substances. The constant amount $3/2\,R \ln 1.0076 + R \ln Q = 2.784$ must be added to the values in Table VII to give $-(F^o - E_0^\circ)/T$ for atomic hydrogen. For example, the value for 298.1°K. is **23.818** calories per degree per mole.

To eliminate the contribution of nuclear spin the amount $R \ln 2 = 1.378$ should be subtracted, thus giving **22.440** at 298.1°K.

TABLE VII

VALUES OF $\frac{5}{2} R \ln T + R \ln \frac{(2\pi k)^{3/2}}{h^3 N^{5/2}} + R \ln R$

	$^5\ R \ln T - 7.267$		$R \ln 2' - 7.267$		$\frac{5}{2} R \ln T - 7.267$
298.1	21.034	1250	28.154	3200	32.823
300	21.065	1300	28.349	3300	32.976
350	21.831	1400	28.717	3400	33.124
400	22.494	1500	29.060	3500	33.268
450	23.079	1600	29.380	3600	33.408
500	23.603	1700	29.681	3700	33.544
550	24.076	1800	29.965	3800	33.677
600	24.508	1900	30.234	3900	33.806
650	24.906	2000	30.489	4000	33.932
700	25.274	2100	30.731	4100	34.054
750	25.617	2200	30.962	4200	34.174
800	25.937	2300	31.183	4300	34.291
850	26.238	2400	31.394	4400	34.405
900	26.522	2500	31.597	4500	34.517
950	26.791	2600	31.792	4600	34.626
1000	27.046	2700	31.979	4700	34.733
1050	27.288	2800	32.160	4800	34.837
1100	27.519	2900	32.334	4900	34.940
1150	27.740	3000	32.503	5000	35.040
1200	27.951	3100	32.665		

For the reaction $H_2 = 2H$, values of $\Delta(F^o - E_0^\circ)/T$ may be obtained from the above tables.

$$\frac{\Delta F^\circ}{T} = -R \ln K = \Delta\left(\frac{F^\circ - E_0^\circ}{T}\right) + \Delta E_0^\circ$$

where $K = [H]^2/[H_2]$.

ΔE_0° has been evaluated by a number of authors from vibration bands which have been observed to dissociate in the case of one of the higher electronic levels. A knowledge of the molecular and atomic excitation energy completes the necessary information. The basis of such calculations has been discussed by Birge and Sponer[24] and a summary of recent work has been given by Birge.[25]

The most reliable value is that given by Richardson and Davidson,[26] namely, 4.46 ± 0.04 volt electrons or since 1 volt electron = 23,059 calories per mole, $\Delta E_0^\circ = 102{,}800 \pm 1000$ calories per mole.

Bichowsky and Copeland[27] have calorimetrically determined the ΔH of the above reaction to be 105,000 ± 3500 calories per mole at room temperature. With the assistance of Table III it is found that this should be decreased by 940 calories in order to obtain ΔE_0°. Thus $\Delta E_0^\circ = 104{,}000 \pm 3500$ calories in satisfactory agreement with the spectroscopic value.

Using the value $\Delta E_0^\circ = 102{,}800 \pm 1000$ calories per mole with Tables VI and VII, the values given in Table VIII have been computed.

TABLE VIII

FREE ENERGY OF DISSOCIATION OF HYDROGEN

T, degrees absolute	$-\Delta\left(\frac{F^\circ - E_0^\circ}{T}\right)$ Calories per degree	$\frac{\Delta F}{T}$	$K = e^{-\Delta F/RT} = [H]^2/[H_2]$
298.1	20.445	324.406	$(1.2 \pm 4.7) \times 10^{-71}$
500	22.054	183.546	$(7.6 \pm 12) \times 10^{-41}$
1000	24.153	78.647	$(6.4 \pm 3.8) \times 10^{-18}$
1500	25.328	3.205	$(3.6 \pm 1.3) \times 10^{-10}$
2000	26.106	25.294	$(2.96 \pm 0.77) \times 10^{-6}$
2500	26.662	14.458	$(6.92 \pm 1.4) \times 10^{-4}$
3000	27.060	7.207	$(2.66 \pm 0.45) \times 10^{-2}$
3500	27.384	1.987	$(3.68 \pm 0.52) \times 10^{-1}$
4000	27.656	−1.956	2.68 ± 0.32
5000	28.064	−7.504	43.7 ± 4.4

Additional values may be calculated similarly from the data given in Tables VI and VII. The estimate of the accuracy is based on the assumption that the ΔE_0° is reliable to 0.04 volt electrons. When a more accurate value of ΔE_0° becomes available, a very simple correction may be applied.

In Table IX the values of the percentage dissociation at one atmosphere pressure are given: percentage dissociation = $100\sqrt{K/(K + 4P)}$, where P = total pressure. The values given by previous authors have been included for comparison.

We have previously mentioned the good agreement between the calculated values and those obtained by Langmuir. This would not be so if the spin effects were not properly considered. For example, neglect of the electron spin multiplicity in the hydrogen atom would decrease all the

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[24] Birge and Sponer, *Phys. Rev.*, 28, 259 (1926).

[25] Birge, *Trans. Faraday Soc.*, 25, 707 (1929).

[26] Richardson and Davidson, *Proc. Roy. Soc.*, (London), 123A, 466 (1929).

[27] Bichowsky and Copeland, THIS JOURNAL, 50, 1315 (1928).

TABLE IX

PERCENTAGE OP HYDROGEN DISSOCIATED AT A TOTAL PRESSURE OP ONE ATMOSPHERE

T, degrees absolute	This author	Langmuir[28b] 1915	Saha[28] 1920	Duffendach[29] 1922	Edgar* 1923	Lewis and Randall,[31] 1923	Wohl[32] 1924
298.1	$(1.8 \pm 6.6) \times 10^{-34}$	..	..	....		..	..
500	$(4.4 \pm 6.7) \times 10^{-19}$	..	..	....	..	..	..
1000	$(1.3 \pm 0.8) \times 10^{-7}$	..	..	....	..	..	..
1500	$(9.5 \pm 3.4) \times 10^{-4}$	..	..	1900×10^{-4}	..	..	..
2000	0.086 ± 0.011	0.17	1	6.5	0.63	0.89	0.83
2500	1.31 ± 0.13	1.6	11	59	5.95	..	..
3000	8.1 ± 0.65	7.2	46	....	26	..	..
3500	29.7 ± 1.1	21	85	....	.	70	..
4000	63.3 ± 2.2	..	96.5	....	..	..	..
5000	95.7 ± 0.1	..	100	....	..		..

calculated dissociation constants by a factor of four. This same effect has been even more definitely demonstrated by Gibson and Heitler[21] in the case of the dissociation of iodine.

The agreement also supports the statement of Gibson and Heitler that nuclear spin effects cancel in chemical reactions and can thus be ignored. Although this factor was not ignored in the above calculation, the results above ordinary temperatures would be identical if it had been, since the limiting contribution to the free energy of both reactant and product is $-RT \ln 4$.

It is evident that the results of spectroscopy will permit the determination of chemical equilibria involving simple molecules with an accuracy not attainable by previous experimental methods.

Summary

The band spectrum data of the hydrogen molecule have been used to illustrate the exact calculation of several thermodynamic properties.

The relative amounts of ortho and para hydrogen molecules under equilibrium conditions have been given over the significant temperature range with high accuracy.

The energy contents and heat capacities of pure para hydrogen, pure ortho hydrogen, the equilibrium mixture and the mixture consisting of one part para to three parts of ortho hydrogen have been calculated over the range from 0° to 298.1°K.

The free energy of the reaction $H_2 = 2H$ has been calculated at various temperatures up to 5000°K. The equilibrium constants and percentage

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[28] Saha, *Phil.* Mag., 40, 472 (1920).

[29] Duffendach, Science, 55, 210 (1922); *Phys. Rev.*, 20, 665 (1922).

[30] Edgar, THIS JOURNAL, 45, 673 (1923).

[31] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 471.

[32] Wohl. *Z. Elektrochem.*, 30, 49 (1924).

dissociation have been given and comparison has been made with the results published by others. The fractions dissociated as obtained from band spectrum data alone are shown to be in good agreement with those given by Langmuir on the basis of the amount of heat conducted from a hot filament in an atmosphere of hydrogen.

Tables of the free energy function for hydrogen have been given for temperatures up to 5000°K. These will be useful in connection with chemical reactions in which hydrogen takes part, and will be followed by the publication of similar tables for other substances.

The absolute entropy of hydrogen was found to be 33.98 calories per degree per mole. The entropy which should be given by the ordinary application of the third law of thermodynamics, including the usual Debye extrapolation below the temperatures of liquid hydrogen, is shown to be 29.59 E.U. This is in close agreement with the experimental value 29.7 or 29.6 depending on whether the equation of Berthelot or that of van der Waals, is used in correcting for gas imperfection. The theoretical value of 29.59 E.U. is obtained from the assumption that the lowest levels of ortho and para hydrogen, with their combined total of ten quantum species, are present in the solid state as a perfect solution. The relative amounts are those determined by the room temperature equilibrium of ortho and para hydrogen. This is one of the best proofs of the third law of thermodynamics.

The effect of nuclear spin on the entropies obtained from the third law has been discussed. This question is of first importance in the practical application of the third law since nearly all elements have a nuclear spin and it contributes a considerable amount of entropy. It is concluded that the portion of the absolute entropy resulting from nuclear spin will usually persist to temperatures below those at which measurements are ordinarily made. There is reason to believe that hydrogen will prove to be the one exception to the above statement but further experiments are necessary to lend weight to this.

Gibson and Heitler have shown that the effect of nuclear spin, like the isotope effect, cancels in reactions. While this is a high temperature approximation, the sense of our above statements is that a few degrees absolute is usually a sufficiently high temperature to effect cancellation. This being so the ordinary method of applying the third law automatically corrects for the neglect of nuclear spin entropy through cancellation in the chemical reaction concerned. This explains the previous successful tests of the third law.

In the case of hydrogen a few degrees or even a hundred degrees absolute is not sufficient to approach the limiting case. Thus in order to obtain an entropy value for hydrogen which may be used in combination with those obtained by the ordinary application of the third law to other substances, we may adopt the artifice of subtracting the limiting spin entropy from the known absolute entropy, giving the value **33.98** $-$ R ln 4 $=$ **31.23 E.U.**

This is in agreement with the fact that the ordinary, and incorrect, application of the third law to hydrogen has, in general led to discrepancies which would be reduced by the use of this value.

We wish to emphasize that while some uncertainty may remain as to the effect of nuclear spin on other substances, no reasonable doubt exists as to the value of the entropy of hydrogen.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

A STUDY OF THE CADMIUM–LEAD CHLORIDE VOLTAIC CELL[1]

BY RUDOLF J. PRIEPKE AND WARREN C. VOSBURGH

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The difference between two values reported for the electromotive force of the cell

$$\mathrm{Cd(Hg)} \mid \mathrm{CdCl_2\,2.5H_2O\ (sat.)} \mid \mathrm{CdCl_2\,2.5H_2O\ (sat.),\ PbCl_2\ (sat.)} \mid \mathrm{Pb(Hg)} \qquad (1)$$

namely 0.1408 v.[2] and 0.13859 v.[3] at 25°, respectively, is too great to be attributed to experimental error.

The value for Cell 1 can be calculated from the values of the cells

$$\mathrm{Cd(Hg)} \mid \mathrm{CdCl_2\,2.5H_2O\ (sat.)} \mid \mathrm{CdCl_2\,2.5H_2O\ (sat.),\ Hg_2Cl_2\ (sat.)} \mid \mathrm{Hg} \qquad (2)$$

$$\mathrm{Pb(Hg)} \mid \mathrm{PbCl_2\ (sat.)} \mid \mathrm{PbCl_2\ (sat.),\ Hg_2Cl_2\ (sat.)} \mid \mathrm{Hg} \qquad (3)$$

Lipscomb and Hulett[4] found for Cell 2 the value $E_{25} = 0.67080$ v. For Cell **3** Gerke[5] found the value $E_{25} = 0.5299$ v. Calculating the electromotive force of Cell **1** from these values gives a result which agrees well with the value found by Obata. Cell **3** and the similar cell with a solid lead electrode have been studied by numerous other investigators.[6] Values calculated for Cell 1 from the results for Cell 3 obtained by some of these investigators are in better agreement with Vosburgh's value. Cells **1** and **3** have therefore been studied further.

The electromotive force–temperature curve of Vosburgh's cell shows a transition point at 26° which does not correspond to the transition point of cadmium chloride. An explanation of this was sought also.

[1] Taken from a thesis presented by Rudolf J. Priepke in partial fulfilment of the requirements for the degree of Master of Arts at Duke University in June, 1930.

[2] Obata, *Proc. Phys. Math. Soc. Japan,* [3] **3,** 64, 136 (1921).

[3] Vosburgh, THIS JOURNAL, **49,** 2222 (1927).

[4] Lipscomb and Hulett, *ibid.*, **38,** 20 (1916).

[5] Gerke, *ibid.*, **44,** 1698 (1922).

[6] (a) Babinski, Dissertation, Leipzig (1906); (b) Timofejew, *Z. physik. Chem.*, **78,** 310 (1912); (c) Brönsted, *Z. Electrochem.*, **19,** 754 (1913); (d) Lewis and Brighton, THIS JOURNAL, **39,** 1906 (1917); (e) Gunther, *Z. Electrochem.*, **23,** 197 (1917); (f) Krahmer, *ibid.*, **26,** 97 (1920); (g) Getman, THIS JOURNAL, **40,** 611 (1918).

Preparation of Materials

Mercury was purified by washing with mercurous nitrate solution and distilling under reduced pressure in a current of air.

Water for the preparation of materials was redistilled from alkaline permanganate. Water for the electrolyte solutions was redistilled a second time in an all-silica still.

Three preparations of mercurous chloride were used. Preparation 1 was made by adding dilute hydrochloric acid slowly to mercurous nitrate solution. Preparation 2 was made by adding mercurous nitrate solution to dilute hydrochloric acid. Preparation 3 was made by a modification of the electrolytic method of Hulett.[4] All three preparations were digested under dilute hydrochloric acid at a temperature near the boiling point for at least eight hours.

Lead chloride was precipitated by adding a solution of recrystallized lead nitrate drop by drop to a solution of redistilled hydrochloric acid.

Baker's c. P. cadmium chloride and potassium chloride were recrystallized from redistilled water.

Lead amalgam was made electrolytically from purified mercury and lead chloride and contained approximately 6% of lead.

To make cadmium amalgam, cadmium was electrolyzed from c. P. metal sticks into commercial redistilled mercury through cadmium sulfate solution. From the amalgam thus formed the cadmium was again electrolyzed into purified mercury, forming a 12% amalgam. This was diluted with mercury to make a 10% amalgam.[7]

Experimental

Preparation of Cells.—The cells were set up in glass H-vessels 16 cm. high and 5.5 cm. wide. The tubes had an inside diameter of 10 mm. In the preparation of Cells 2A and 2B, the mercurous chloride was filtered in a Gooch crucible and mixed in an agate mortar with crystals of cadmium chloride. This paste was transferred to a separatory funnel and washed several times in an atmosphere of nitrogen with the electrolyte solution. It was then put into the cell vessel on top of the mercury, the end of the separatory funnel being kept under the surface of some electrolyte solution above the mercury. Cadmium chloride crystals were then placed above the paste. The melted amalgam was put into the vessel by means of a heated glass tube, and the surface washed with some slightly acidified electrolyte solution to remove cadmium oxide. Then the surface was washed several times with electrolyte solution and finally crystals of cadmium chloride and electrolyte were put on top of it. The vessels were filled to the cross arm with electrolyte and closed with paraffin-coated corks. All the other cells (except Cells 3C and 3D, which were prepared without precautions to protect from air) were prepared in a similar manner. In the preparation of Cells 1C, 1D, 1E, 2C, 2D, 3E and 3F the paste was not washed in a separatory funnel. Instead, the cells were alternately evacuated and filled with nitrogen several times. Cells 2E, 2F, 3G and 3H were prepared using both these precautions.

In Cells 3A and 3B saturated lead chloride solution was used as the

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[7] The cadmium amalgam was prepared by Kelly L. Elmore.

electrolyte. In Cells 3G and 3H, 1.0 *N* potassium chloride solution was used. All the other cells contained saturated cadmium chloride solution as the electrolyte. In cells with saturated cadmium chloride solution as the electrolyte, cadmium chloride crystals were mixed with the paste and were present in excess in both arms of the cell.

The cells were kept at 25°, except as otherwise indicated, in an electrically controlled oil thermostat, the temperature of which fluctuated not more than ±0.01° and under favorable conditions not more than ±0.005°. The temperatures are probably correct to within ±0.02°.

Electromotive Force Measurements.—The electromotive forces were measured by means of a calibrated Leeds and Northrup Type K potentiometer. Standard Weston cells Nos. 353–356 and 496 previously described[8] were used as reference standards. They were found to agree within one or two parts in 100,000 with two portable saturated cells certified by the Bureau of Standards.

A number of the cells started with abnormally high electromotive forces. The electromotive forces of such cells decreased continuously over a period of several weeks until finally constant values were obtained. Changes in temperature appeared to hasten the attainment of a constant value. Other cells were practically constant from the beginning. Table I shows the initial and final constant values of cells of each of the three types. In most cases the constant values of duplicate cells agreed to within 0.1 mv., but in two cases duplicates differed by 0.6 mv. The latter were given less weight in selecting the final values.

Of the three types of cells, the calomel standard cell of Lipscomb and Hulett, Cell 2, was the easiest to reproduce. The quality of Cell 3 depended somewhat on the electrolyte used, potassium chloride giving the best results. When no electrolyte other than the lead chloride was used, the electromotive force was about 1 mv. too high, and the cells did not agree well.

Table I

Electromotive Forces at 25°

	E. m. f., v.			E. m. f., v		
Cells	Initial	Constant	Cells	Initial	Constant	Electrolyte
1A, 1B	0.1393	0.1405[a]	3A, 3B	0.5315	0.5310	$PbCl_2$, sat.
1C	.1365	.1400	3C, 3D	.5337	.5301	$CdCl_2$, sat.
1D, 1E	.1345	.1406	3E, 3F	.5366	.5301	$CdCl_2$, sat.
2A, 2B	.6706	.6707	3G, 3H	.5298	.5297	KCl, 1 N
2C, 2D	.6740	.6703				
2E, 2F	.6706	.6706				

[a] After a number of later temperature changes Cell 1A assumed the value 0.1407 v. Cell 1B was variable after a series of temperature changes.

Two temperature coefficient determinations were made, the first using a limited number of cells and the second all cells which had come to equi-

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[8] Vosburgh, This Journal, 47, 1257 (1925); **49,** 85 (1927).

TABLE II

ELECTROMOTIVE FORCES AT VARIOUS TEMPERATURES

Temp., °C.	Cells 1A, 1B, v.	Cell[d] 1A, v.	Cells 2A, 2B, v.	Cells 2E, 2F, v.	Cells 3G, 3H, v.
25	0.14052	0.14072	0.67063	0.67062	0.52974
20	.14166	.14185	.67108	.67108	.52907
17	....	.14248	.67130	.67128	.52862
20	....	.14185	.67108	.67106	.52888
25	.14055	.14069	.67060	.67058	.52973
30	.13933	.13945	.67007	.67007	.53040
35	.13854	.13854	.66995	.66989	.53110
40	.13927	.13925	.67135	.67136	.53178
35	.13857	....	....	....	....
30[a]	.13787	.13786	.66857	.66851	.53038
25[a]	.13716	.1365[e]	.67131[e]	.66706	.52963
25[b]	.14075[c]	.1407	.67067	.67059	....

[a] Cells 1 and 2 were metastable at these temperatures. [b] These values were obtained after stable equilibrium had been reattained. [c] This value was for Cell 1A. Cell 1B did not come back to a definite equilibrium. [d] This is a second determination of the temperature coefficient of Cell 1A. [e] One leg of each of these cells became stable while the other remained metastable.

librium. Beginning at 25° the temperature was changed as indicated in the first column of Table II. Usually three days or more were allowed for the cells to come to equilibrium at each temperature. In a few cases, when measurements at intervals showed no change taking place, less time was allowed. Electromotive force measurements were made every day. The results are given in Table II.

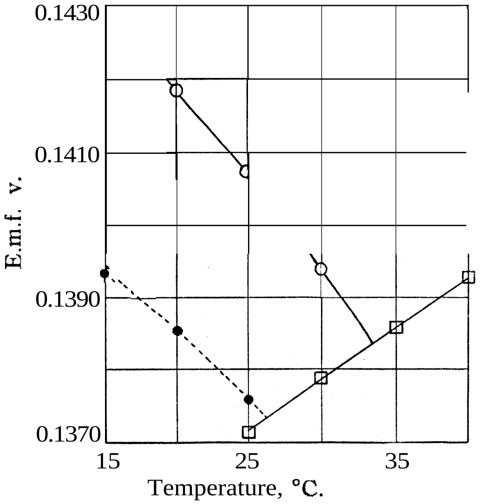

Fig. 1.—Variation of the electromotive force of Cell 1 with temperature. The circles are values of Cell 1 obtained in this investigation. The dotted curve gives the values previously found by Vosburgh. The squares are points at which Vosburgh's cell and Cell 1 were in close agreement and represent the values of the electromotive force when monohydrated cadmium chloride is the solid phase.

Since cadmium chloride changes from the hemipentahydrate to the monohydrate at about 34° there is a sharp change of slope at that point in the electromotive force–temperature curve of the cells with cadmium as illustrated by Fig. 1. On decreasing the temperature, the monohydrate did not change back to the hemipentahydrate immediately, sometimes not even at 25°. To hasten this change, after the first temperature coefficient determination, the cells were put into an ice–salt mixture for a day. After the second determination, instead of this treatment the cells were opened and seeded with crystals of the hemipentahydrate. The latter method is much more effective. The electromotive forces then returned to the values for the stable cells at 25°, except in the case of Cell 113 which, after being cooled, became variable.

Discussion

The value found for Cell 2, $E_{25} = 0.6706$ v., was about 0.2 mv. lower than the value given by Lipscomb and Hulett.[4] This, while not a serious disagreement, may perhaps have been caused by the digestion of the mercurous chloride. It has been shown[9] that digestion of mercurous sulfate gives a more stable preparation, leading to lower and more reproducible results when used in Weston cells. The same was found to be true in the case of lead dioxide.[10]

Cell 2 became metastable when the temperature was raised above 34° and then cooled again. The metastable cells readily assumed their normal value at 25° on being seeded with hemipentahydrate crystals or subjected to cooling treatment. The electromotive force of Cell 2 between 20 and 30° is given by the formula

$$E = 0.6706 - 0.000102\,(t - 25) - 0.0000025\,(t - 25)^2$$

the temperature coefficients being those found by Lipscomb and Hulett. From 34 to 40° and for the metastable cell between 25 and 34° the electromotive force is given within 0.1 mv. by the formula

$$E = 0.6699 + 0.000284\,(t - 35)$$

Five cells of the type of Cell 1 were made which gave good results. Three of them did not come to equilibrium until the middle of the temperature coefficient determination, but their values in the metastable state as well as their values in the final stable state at 25° were in good agreement with the other two cells.

The values at different temperatures of Cell 1A, which was subjected to both temperature coefficient determinations, are given in Table III, together with those calculated from the formula given by Obata.[2]

TABLE III

ELECTROMOTIVE FORCE OF CELL 1 AT DIFFERENT TEMPERATURES

Temp., °C.	17	20	25	30
Cell 1A, v.	0.14248	0.14185	0.14072	0.13945
Obata, v.	.14243	.14186	.14080	.13956

When Cell 1 has monohydrated cadmium chloride as the solid phase in equilibrium (or metastable equilibrium) with the electrolyte, the re-

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[9] Vosburgh, THIS JOURNAL, 46, 104 (1924).

[10] Vosburgh and Craig, *ibid.* 51, 2012 (1929).

lation between the electromotive force and the temperature is practically linear. Table IV gives the electromotive force at different temperatures of Cell 1 of this investigation with monohydrate crystals together with those calculated from the values given by Vosburgh[3] for his cell under the same conditions.

TABLE IV

ELECTROMOTIVE FORCE OF CELL 1 WITH MONOWDRATE CRYSTALS

Temp., °C.	25	30	35	40
E. m. f., Cell 1, v.	0.13716[a]	0.13784[b]	0.13850[b]	0.13918[b]
Vosburgh, v.[c]	.13716	.13788	.13857	.13927

[a] Cells 1A and 1B. [b] Cells 1A, 1B, 1D and 1E. [c] It is to be noted that Vosburgh used an amalgam containing lead. His values have been corrected as indicated in his paper (Ref. 3) and the values given here apply to a cell with pure cadmium amalgam, and so are comparable with the values of Cell 1.

The data in Tables III and IV are plotted in Fig. 1. The tables and figure show that the values of Cell 1 agree with Obata's value rather than with Vosburgh's from 17 to 30°. When the monohydrated cadmium chloride is the solid phase they agree well with the values given by Vosburgh for his cell when in a similar condition. The cadmium chloride in Vosburgh's cell must have been in some unknown metastable state before his temperature coefficient determination. This would account for the transition point being at 26° instead of at 34°. An attempt to duplicate Vosburgh's cells as they were before carrying above the transition point was not successful.

Of the cells of the type of Cell 3, Cells 3C, 3D, 3F, 3G and 3H gave the best results. Table V gives the electromotive forces of these cells at different temperatures, together with the values calculated from Gerke's value[5] with his temperature coefficient. The line marked "Calcd. I" gives the values calculated by subtracting the value of Cell 1 from the corresponding value of Cell 2. The line marked "Calcd. II" gives the values calculated in the same way from the same cells with monohydrated cadmium chloride as the solid phase.

TABLE V

ELECTROMOTIVE FORCE OF CELL 3 AT DIFFERENT TEMPERATURES

Temp., °C.	20	25	30	35	40
Cells 3C, 3D, v.	0.53006	0.53030	0.53097	0.53144	0.53206
Cells 3F, 3G, 3H, v.	.52905	.52971	.53037	.53114	.53182
Gerke, v.	.5293	.5299	.5306	.5312	.5318
Calcd. I, v.	.52923	.52989	.53062	....	....
Calcd. II, v.	....	.52990	.53070	.53142	.53217

Summary

The following cells have been set up and their electromotive forces and temperature coefficients measured.

$$\mathrm{Cd(Hg)} \mid \mathrm{CdCl_2{\cdot}2.5H_2O\ (sat.)} \mid \mathrm{CdCl_2{\cdot}2.5H_2O\ (sat.),\ PbCl_2} \mid \mathrm{Pb(Hg)} \quad (1)$$
$$\mathrm{Cd(Hg)} \mid \mathrm{CdCl_2{\cdot}2.5H_2O\ (sat.)} \mid \mathrm{CdCl_2{\cdot}2.5H_2O\ (sat.),\ Hg_2Cl_2} \mid \mathrm{Hg} \quad (2)$$
$$\mathrm{Pb(Hg)} \mid \mathrm{PbCl_2\ (sat.)} \mid \mathrm{PbCl_2\ (sat.),\ Hg_2Cl_2} \mid \mathrm{Hg} \quad (3)$$

When hemipentahydrated cadmium chloride was the solid salt in equilibrium with the electrolyte in Cell 1, the values were in good agreement with the values found by Obata. When monohydrated cadmium chloride was the solid salt in equilibrium (or metastable equilibrium) with the electrolyte, the values were in good agreement with those found by Vosburgh when his cells had the monohydrate as the solid phase.

A value only slightly lower than that of Lipscomb and Hulett was found for Cell 2.

From the values for Cells 1 and 2 a value for Cell 3 was calculated which agreed with the observed values for Cell 3 and with Gerke's values for this cell. Of the three this cell was the most difficult to reproduce.

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

KINETICS OF THE ACETYLENE–OXYGEN REACTION

BY ROBERT SPENCE AND GEORGE B. KISTIAKOWSKY

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Although of extraordinary technical and general interest, the problem of the mechanism of hydrocarbon combustion has yielded very little exact, reproducible information despite numerous investigations, principally owing to the complexity of the process and the consequent possibility of considerable variation in the course of reaction with changing conditions. However, the results of more recent experimental work on the slow oxidations of gaseous hydrocarbons have led several workers to postulate a chain mechanism.[1] Thus, it was found that in vessels packed with pieces of the same material as that of the containing walls, the reaction velocity is slower and the products are, in general, somewhat different. An even more direct evidence in favor of this hypothesis has been obtained by Spence and Taylor,[2] who showed that small amounts of ozone introduced into a stream of slowly reacting oxygen and ethylene accelerate the rate of reaction between the latter. In the few cases that have been studied, the reaction kinetics appear to be somewhat unusual and favor the assumption of a chain mechanism. Thompson and Hinshelwood[1] observed that the velocity of the ethylene–oxygen reaction is proportional to a high power of ethylene concentration and is almost independent of oxygen. Very similar

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[1] Pease, THIS JOURNAL, 51, 1839 (1929); Pope, Dykstra and Edgar, *ibid.*, 51, 2203, 2213 (1929); Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), **125A**, 277 (1929); Kistiakowsky and Lenher, Nature, 124, 761 (1929); THIS JOURNAL, 52, 3785 (1930).

[2] Spence and Taylor, *ibid.*, 52, 2399 (1930).

observations have been made with acetylene,[3] hydrogen,[4] higher aliphatic hydrocarbons,[5] and benzene.[6] Hence, it appears that many gaseous hydrocarbon oxidation reactions have common properties and therefore anything which is found true for one of them may very probably apply to other hydrocarbons with little modification.

Since the complexity of the oxidation reaction undoubtedly increases with the size of the hydrocarbon molecule, the authors decided to study the oxidation of that one having the smallest number of atoms, namely, acetylene, which reacts with oxygen at moderate temperatures and thus makes the isolation of unstable intermediary products more probable. Those who have studied this reaction previously employed two methods of attack. Bone and Andrew[3] enclosed various mixtures of oxygen and acetylene at known total pressures in glass bulbs, raised the bulbs to given temperatures for a certain time, then noted the pressure change after cooling to room temperature and finally analyzed samples of the gases. The principal gaseous product was carbon monoxide. In a second series of experiments they employed a flow system, but in this case their reaction vessel was packed with broken porcelain and the gaseous product contained a much larger percentage of carbon dioxide. The work of Kistiakowsky and Lenher[1] on flowing mixtures of acetylene and oxygen showed that Bone and Andrew's bulb reactions were of the homogeneous kind, while the packed tube reactions giving a larger proportion of carbon dioxide were principally of the wall variety. The authors decided to use a circulating system for their experiments because it combines the advantages of the previous static and flow methods. In the apparatus finally adopted, gases could be admitted in any given amounts up to atmospheric pressure, could be circulated through the furnace at a given rate and the total pressure in the apparatus noted at intervals. A U-tube cooled in carbon dioxide and ether removed all condensible products immediately on leaving the furnace and these could be analyzed after the experiment, together with a sample of the gaseous products.

Circulating Pump.—Mixtures of acetylene and oxygen are extremely sensitive and will explode with great violence on the slightest provocation. A circulating pump necessitates considerable friction, particularly in valves, with the consequent possibility of electrical discharges. In the first apparatus the circulating pump was equipped with mercury non-return valves but these would detonate the gas mixture without warning after working satisfactorily for as many as six experiments. Then an all-glass valve was evolved, similar in design to that shown in Fig. 1. A

[3] Kistiakowsky and Lenher, Ref. 1; Bone and Andrew, *J. Chem. Soc.*, *87*, 1232 (1905).

[4] Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), 122,615 (1929)

[5] Lewis, *J. Chem. Soc.*, 58 (1930).

[6] Fort and Hinshelwood, *Proc. Roy. Soc.* (London), **127A,** 218 (1930).

flexible glass plate, no more than 0.002 in. thick was held against the flat, ground end of a capillary tube by a fine glass rod sealed into a side tube. A non-return valve of this type is efficient, sturdy and simple to make. However, despite the fact that practically all mechanical friction had been eliminated, explosions still resulted. Here the source of the trouble seemed to be the "Armstrong effect" of dry gases streaming from a narrow jet, giving an electrical charge to the jet which eventually discharged to the glass plate, the latter having meanwhile taken the opposite charge from the gases. In the design eventually adopted, and which proved to be quite successful (Fig. 1), the tip of the capillary jet was coated with a mirror of platinum and the glass plate replaced by a thin plate of beaten platinum foil welded to a tungsten wire sealed into the side tube. The end of the tungsten wire was connected to earth and all possibility of an accumulation of electrical charge removed. While not so efficient as the glass or mercury valves the new type allowed of a reasonable rate of pumping, which was all that was required. Attempts were made to localize explosions in order to prevent complete destruction of the apparatus which inevitably ensued when all the gas mixture was detonated. Tubes containing fairly tight wads of cotton wool placed at either end of the circulating pump proved to be very efficient and while they were in use no explosion spread beyond the valves of the circulating pump. Fig. 1 illustrates the arrangement of the circulating pump. Four valves were connected to the steel pump barrel by two glass tubes longer than a barometric column. These columns were filled with mercury which could be given an oscillating motion by movement of the piston in the steel cylinder. A packing composed of a mixture of stopcock grease, asbestos pulp and graphite, enclosed in the piston gland, effectively prevented any leakage of mercury, while cheesecloth filters placed at the foot of the mercury columns helped to keep the mercury free from grease contamination.

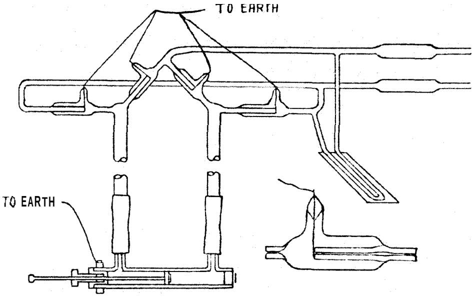

Fig. **1.—Circulating pump and** valve.

Main Apparatus.—By far the larger part of the total gas enclosed in the apparatus was contained in two glass bulbs, each of 200 cc. capacity, placed next to the pump. A large very stout wooden cover surrounded the bulbs, which were connected to the cotton wool safety tubes on either end of the pump. The gases could be circulated around the pump and bulbs to ensure thorough mixing, then admitted to the furnace circuit which had previously been evacuated. The furnace consisted of a pyrex glass tube of 98 cc. capacity into which was sealed a tube containing a thermocouple. Immediately on leaving the furnace, the gases passed into a U-tube cooled in a carbon dioxide–ether mixture and which was connected to the apparatus by two ground-glass joints sealed with piceine wax. To ensure uniformity of conditions before and after the reaction, another U-tube cooled in carbon dioxide–ether mixture was placed immediately before the furnace, while the pressure of the gases entering this U-tube was measured on a mercury manometer having a barometer attached to the same scale.

Purification of the Gases.—Oxygen from a tank was dried in a sulfuric acid wash bottle, then passed into a storage bulb via a U-tube immersed in a solid carbon dioxide-ether mixture. Acetylene, obtained from a small Prestolite tank, was bubbled through water, a mixture of cupric and ferric chloride solutions, caustic potash and finally passed over calcium chloride into a vessel cooled in liquid air, where it condensed to a white solid. Inert gases were removed by evacuation, the solid was distilled from a carbon dioxide-ether bath and the middle fraction collected in a storage bulb. After further solidification and evacuation, the acetylene was again allowed to evaporate into the bulb, where it was ready for use.

Calibration of the Apparatus.—The volume of the apparatus and its parts was determined by admitting gas at known pressure and volume into the evacuated apparatus and reading the pressure.

Volume of circulating pump and capacity bulbs	550 cc.
Volume of furnace (cold)	98 cc.
Volume of U-tubes, etc.	26 cc.
Total volume	674 cc.

In order to know the time of contact of the gases with the furnace at the various pressures studied, the U-tube was replaced by two 500-cc. bulbs connected by a stout, wide bore, rubber tubing, containing a strong solution of calcium chloride. The time necessary to transfer 500 cc. of liquid (the levels of the solution in the two bulbs being kept the same) was noted over a large range of pressures and pumping rates and the results were plotted so that the contact period for any given conditions could easily be read off.

Experimental Method.—Before beginning an experiment, the furnace was adjusted to the required temperature, the U-tubes surrounded with carbon dioxide–ether mixtures, and the whole apparatus evacuated. After having shut off the furnace section from the rest of the apparatus, definite amounts of acetylene and oxygen, measured on the manometer, were admitted and circulated for about five minutes to ensure good mixing of the two gases. At this point the necesary stopcocks were turned, bringing the furnace into the circulating system and closing the by-pass. Readings of manometer, barometer, temperature and pumping rate were taken immediately and at given intervals thereafter until the experiment was finished. Upon completion of an experiment, the furnace was again shut off, evacuated, and a sample collected from the remaining gas by a mercury pipet in which it was retained for analysis.

Analysis of the Products.—At the end of an experiment, the U-tube contained a mixture of polymerized glyoxal, formaldehyde, formic acid and water. These were washed out with hot water, in which the polyglyoxal dissolves, a hot solution of the hydrochloride of p-nitrophenylhydrazine added and the mixture filtered through a tared Gooch crucible. After drying and weighing, the crucible was placed in a Soxhlet apparatus and extracted with chloroform. This treatment removed the *p*-nitrophenylhydrazone of formaldehyde and left the *p*-nitrophenylosazone of glyoxal behind. A final drying and weighing gave the weight of formaldehyde and glyoxal. The p-nitrophenylosazone of glyoxal crystallizes from pyridine in long red needles, m. p. 318°. *Anal.* Calcd. for $C_{14}H_{12}O_4N_6$: C, 51.2, H, 3.7. Found: C, 51.35, H. 3.9. In an identical experiment, the condensate was made up to 10 cc. and two 5-cc. portions were titrated with $N/100$ baryta solution, using brom cresol purple as indicator. This gave the amount of formic acid present. The gas collected over mercury was analyzed for acetylene (by fuming sulfuric acid), carbon dioxide, oxygen, carbon monoxide and hydrogen (over heated copper oxide). From these figures, a balance of carbon, before and after the reaction, could be made.

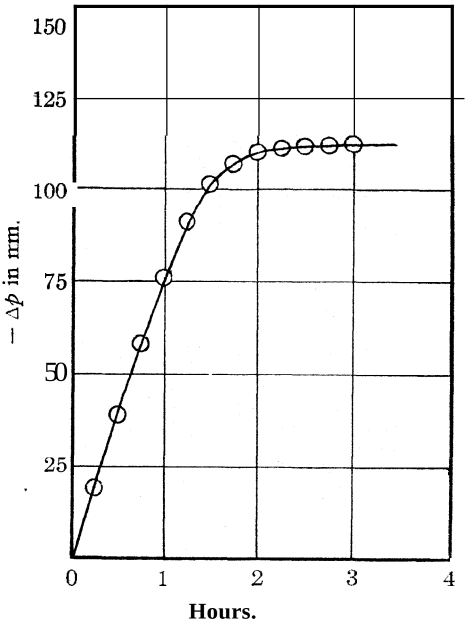

Fig. 2.—$-\Delta p$ curve for a mixture of approx 400 mm C_2H_2 and 100 mm O_2 at 320°, reaction carried to completion

Experimental Part

Figure 2 represents a typical experiment which has been carried to completion and shows the general form of the pressure–time curve. The example shown, however, was not obtained with an apparatus identical with that used in the principal experiments. The results of all the experiments quoted below were plotted in a similar manner and dx/dt, the initial rate of reaction in mm. per minute, obtained by direct measurement.

The Induction Period.—To ascertain the effect of varying rates of pumping on the reaction velocity, series of mixtures of constant composition were circulated at different rates and the reaction velocity determined.

TABLE I

EFFECT OF CONTACT TIME ON REACTION VELOCITY

No.	C_2H_2, mm.	O_2, mm.	Contact time, sec.	dx/dt
32	175.7	192.6	50	0.56
33	173.7	191.3	12	.34
34	173.6	192.6	18	.44
35	173.4	191.4	37	.56

We see that for contact periods greater than about twenty-five seconds, the rate is independent of the pumping Speed. The rapid falling off in reaction rate with higher pumping speeds must be due to the existence of an induction period.

Temperature Coefficient.—Measurements of rates of reaction of given mixtures at different temperatures are given in Table II. In all succeeding experiments the rate of pumping was arranged so as to give a constant contact period of about forty seconds.

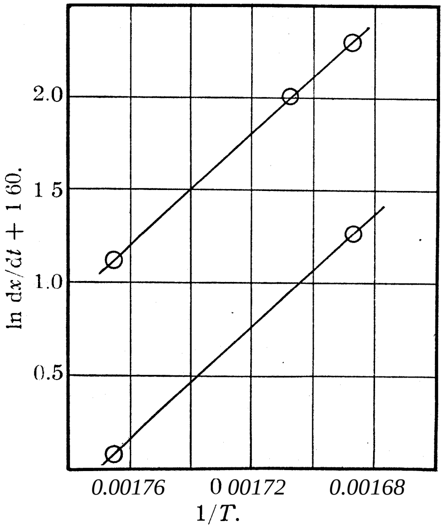

Fig. 3.—Logarithm of rate of reaction plotted against $^1/_{T_{\text{abs}}}$. for two different mixtures.

In Fig. 3 are plotted the logarithms of the reaction velocity against the reciprocal of absolute temperature. Within the narrow temperature interval investigated, the experimental points lie on straight lines and the slope is independent of the composition of the gas mixture, but it is realized that more extended experiments may show a deviation from these results. From the observed temperature coefficient, the activation energy of the reaction is calculated to be 34,700 cal. at 320°.

Influence of Acetylene and Oxygen Concentrations.—Table III gives the initial concentrations of acetylene and oxygen, the pressure decrease at five-minute intervals and the initial rate as measured from each curve. The meaning of K_0 is explained below. All experiments were carried out at 320° with a contact period of forty seconds.

Plotting rate against oxygen concentration, we obtain the four curves

TABLE II

RATE OF REACTION AT DIFFERENT TEMPERATURES

No.	C_2H_2, mm.	01, mm.	T, °C	5 min.	10	Δp 15	20	25	30	dx/dt
2	346.7	86.3	297.0	3.1	6.3	9.4	12.2	150	17.7	0.64
1	3466	86.9	313.5	7.1	14.8	22.5	69.3	363	42.8	1.5
4	347.9	86.9	320.0	10.1	19.8	29.6	39.4	47.2	54.5	2.0
3	173.8	86.3	297.0	1.1	2 0	2.9	3.6	4.4	5.2	0.22
5	173.7	87.2	320.0	3.4	6.9	9.9	12.7	15.3	18 0	0.72

TABLE III

EXPERIMENTS AT 320°

No.	C_2H_2, mm.	O_2, mm.	5 min.	10	Δp 15	20	25	30	dx/dt	K_0
43	61.2	20.6	0.3	0.5	0.9	1.2	1.6	1.9	0.06	1.35
38	70.4	45.9	.5	1.1	1.7	2.2	2.8	3.3	.11	2.21
41	70.6	74.9	.5	1.0	1.6	2.3	2.6	3.1	.10	2.12
42	60.6	88.1	.3	0.7	1.1	1.6	2.1	2.6	.07	2.32
40	61.1	173.9	.2	.5	0.8	1.2	1.5	1.7	.05	2.12
15	174 6	8 5	2 5	4 2	5.8	6.6	7.1	7.4	.48	2.26
18	173.4	17.6	2.4	4.6	6.7	8.6	10.4	11.8	.50	1.68
20	176.7	26.5	2.3	5.1	8.1	11.0	13.5	15.6	.54	1.63
22	175.8	43.5	2.8	6.6	9.8	12.8	16.8	20.0	.64	1.93
30	173.2	70.3	3.3	6.5	9.7	12.7	16.0	19.3	.64	2.09
5	173.7	87.2	3.4	6.9	9.9	12.7	15.3	18.0	.72	2.34
26	172.7	87.3	3.3	6.5	9.4	12.6	14.7	17.0	.66	2.24
35	173.4	191.4	2.4	5.6	8.5	11.4	13.7	16.2	.56	2.15
32	175.7	192.6	2.5	5.6	8.3	11.1	13.5	16.1	.56	2.10
28	176.2	264.1	2.7	5.4	7.9	10.6	12.8	15.3	.53	2.15
29	175.4	303.5	2.4	4.9	7.2	9.4	11.6	14.1	.48	2.05
44	172.1	348.1	..	3.9	..	7.8	..	11.5	.40	1.85
25	173.4	350.1	2.2	4.2	6.4	8.3	10.3	12.2	.44	1.99
10	262.8	1.1	0.3	0.6	0.8	1.0	1.2	1.2	.05	2.88
9	262.3	8.5	2.8	5.1	6.9	8.1	8.9	9.2	.60	2.28
8	262.6	19.2	3.6	7.2	10.5	12.8	14.9	16.2	.78	1.38
6	260.3	26.5	4.3	9.1	13.3	16.5	19.4	22.0	1.00	1.56
11	259.5	90.1	5.2	10.6	16.2	21.3	27.0	33.0	1.08	1.54
12	260.8	175.0	5.3	10.9	17.1	21.9	29.3	32.9	1.16	1.80
16	345.5	9.5	3.2	5.6	7.4	8.5	9.4	9.8	0.66	1.92
17	347.5	17.4	5.9	10.9	14.3	16.5	18.2	19.2	1.34	1.91
19	348.0	26.8	5.5	11.5	15.6	18.9	21.9	23.5	1.28	1.32
21	346.3	44.7	8.5	16.7	24.5	30.6	35.4	37.9	1.72	1.48
23	350.8	72.6	7.5	18.0	27.0	34.8	41.8	46.8	1.80	1.43
4	347.9	86.9	10.1	19.8	29.6	39.4	47.2	54.5	2.00	1.61
36	357.0	129.0	..	20.5	..	40.0	..	58.4	2.04	1.58
37	329.0	13.10	..	18.9	..	36.2	..	52.4	1.86	1.70

shown in Fig. 4. In each case, increase in the oxygen concentration from zero causes an increase in the rate of reaction, until a region is reached where the rate is practically independent of oxygen. Further increase in oxygen concentration somewhat retards the rate of reaction, as illustrated by the negative slope of the latter half of the curves. The experiments indicate that the maximum rate is obtained with mixtures of approximately constant composition irrespective of total pressure. In these optimum mixtures the rate is very nearly proportional to the square of acetylene concentration, as is shown by Table IV, while at relatively low oxygen concentrations the rate is proportional to the first or even lower power of acetylene.

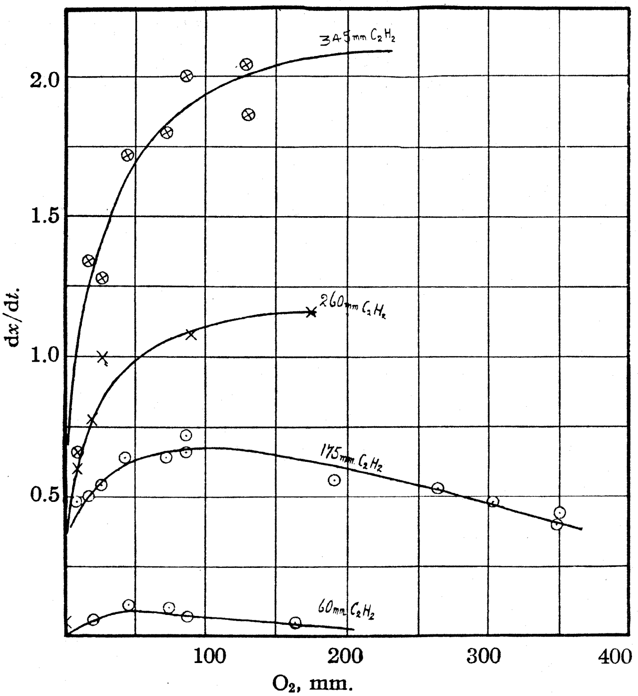

Fig. 4.—Oxygen concentration (for fixed acetylene concentration) plotted against rate of reaction (d*x*/d*t*); temp., 320°.

TABLE IV

DEPENDENCE ON ACETYLENE

C_2H_2, mm.	O_2, mm.	C_2H_2/O_2	Max. d*x*/d*t*	$C_2H_2^2$/d*x*/d*t*
60.0	45.0	1.33	0.09	4.0
175.0	110.0	1.60	0.68	4.4
260.0	180.0	1.44	1.16	5.9
345.0	>230.0	<1.50	>2.10	<5.9

Influence of Nitrogen.—To investigate a possible effect of inert gases an experiment was performed with a large amount of nitrogen present. As appears from Table V, nitrogen has a slight retarding effect which is, however, even less pronounced than that of oxygen when the latter is present in excess.

TABLE V

INFLUENCE ON INERT GASES

No.	N_2, mm.	C_2H_2, mm.	O_2, mm.	Δp 5 min.	10	15	20	25	30	dx/dt
30		173.2	70.3	3.3	6.5	9.7	12.7	16.0	19.3	0.64
31	275.0	175.4	08.6	3.0	5.6	8.4	11.2	13.7	16.2	.56
44		173.3	348.1	...	3.9	...	7.8	..	11.5	.40

Products of the Reaction.—Table VI gives typical results of an analysis of the reaction products. Several sets of such determinations have been carried out on different reacting mixtures but. owing probably to uncertainties of the analysis, no systematic variations in the composition of the products could be detected.

TABLE VI

ANALYSIS OF REACTION PRODUCTS AND CARBON BALANCE

Expt. No. 36; C_2H_2, 357.0 mm.; O_2, 129.0 mm.; dx/dt, 2.04; time, 1 hour

Product	Amount	G. atoms C × 10^3	Gm. atoms C × 10^3 at beginning
$C_2H_2O_2$	0.0227 g.	0.783	
HCHO	.0163 g.	.545	
HCOOH	.0173 g.	.376	
C_2H_2	75.03%	19.180	23.960
CO_2	1.43	0.182	
O_2	7.71		
H_2	.....		
CO	21.90	2.798	
Totals		23.864	23.960

The iodine test gave no indication of the presence of a per-acid in the condensate.

Discussion of Results

The experiments here presented show that oxidation of acetylene can proceed at a perfectly reproducible rate and has well-defined kinetics. The reaction would, therefore, seem to lend itself readily to kinetic treatment. However, any theory of the reaction mechanism would have to account not only for the dependence of the rate—as measured by the manometer—on the concentrations of the reactants, but also for such things as the presence of an induction period and the fate of the intermediate products. It is in the attempt to bring all these phenomena together in one theory that the chief difficulty is encountered.

It seems fairly certain that the induction period is an inherent part of the reaction and is not due to impurities. Thus, Kistiakowsky and Lenher, working with a different method and using considerably less purified gases than in the present work, observed that the lower the temperature at which the reaction proceeded, the longer was the induction period. Using contact times of fifty to two hundred seconds, they failed to notice an induction period at 313°—the highest temperature then studied. This present research, however, shows that an induction period is present even at 320° but is of much shorter duration. The two sets of experiments agree well together and indicate that the length of the induction period is roughly, at least, inversely proportional to the rate of reaction. These facts, together with the character of the present experimental method—a continuous circulation of the gases with removal of condensible products—make it most probable that the induction period is caused by a gradual accumulation of some condensible substance which is necessary for the oxidation of acetylene to acquire its full rate. Since the induction period is of considerable duration, this catalytic substance must possess some degree of stability at the temperatures employed and it thus becomes very probable that it can be identified as one or all of the three condensible intermediate products described above: glyoxal, formaldehyde or formic acid. Although a definite proof of this conclusion is still lacking, some evidence can be brought forward to show that formaldehyde at least must take an active part in the acetylene reaction. According to the theory of Bone[3] formaldehyde is not a by-product but one of the main stages in the oxidation of acetylene, which seems most plausible to the present writers. Furthermore, the experiments of Askey[7] show that mixtures of pure formaldehyde and oxygen are quite stable at 320°, the time of half reaction being of the order of one hour. Thus with a contact time of less than a minute, one should expect to find all the reacted acetylene in the form of formaldehyde. Instead, it is found that the major part of the formaldehyde is oxidized further into formic acid, carbon monoxide and water, its stationary concentration in the reacting mixture being attained in less than a minute at 310° according to experiments of Kistiakowsky and Lenher.[1] This means that in presence of acetylene, formaldehyde is oxidized some hundred times faster than when alone. Owing to lack of experimental data, no similar comparison can be made in the case of glyoxal and formic acid.

The induction period and the behavior of formaldehyde lend additional evidence in favor of a chain mechanism of acetylene oxidation. There is a large series of possible mechanisms for this reaction. The simplest, which does not involve any unidentified intermediate products

$$\begin{aligned} C_2H_2 + O_2 &\longrightarrow C_2H_2O_2 \\ C_2H_2O_2 &\longrightarrow CO + HCHO \\ HCHO + O_2 &\longrightarrow CO_2 + H_2O \end{aligned}$$

must, however, be neglected, since it accounts neither for the observed dependence of the rate on the reactant concentration, nor for the induction period, the oxidation of formaldehdye, nor the presence of chains. Several other schemes involving the least possible number of intermediate reactants were tried and it was found that mechanisms involving, in addition to the substances actually isolated, a compound of the per-acid or per-

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[7] Askey, THIS JOURNAL, **52**, 974 (1930).

oxide type such as have been identified in many other oxidations, led to kinetic equations which could be made to reproduce the general trend of the experimental results. Schemes involving oxygen atoms were, in general, unsatisfactory. The equations derived from the per-acid theory, however, necessitated the assumption of chains sufficiently long that the primary reaction between acetylene and oxygen became insignificant in the total balance of reaction—in agreement with the observed retarding effect of the walls. On the other hand, assuming that each molecule of formaldehyde or glyoxal causes the oxidation of only one or two acetylene molecules, it can be calculated—from the amounts of the intermediary products recovered in the trap—that the chain length, *i. e.*, the number of acetylene molecules oxidized as the result of one primary reaction, does not exceed three to six. To reconcile these conclusions is difficult and it seemed to the writers that, until more experimental data are accumulated, an attempt to set up a detailed theory of the reaction mechanism would be premature. The constant K_0 of Table III was calculated therefore with the aid of an empirical equation

$$\frac{dx}{dt} = K_0 \frac{[C_2H_2]^2[O_2] + 3.5\,[C_2H_2]^2}{0.9\,[O_2] + 0.25\,\frac{[O_2]^2}{[C_2H_2]} + 0.0029\,\frac{[C_2H_2]^2}{[O_2]}}$$

which represents the observations reasonably well.

One of the authors (R. S.) wishes to express his indebtedness to the Commonwealth Fund for a Fellowship which enabled him to take part in this research.

Summary

1. The slow oxidation of acetylene has been studied by a circulation method allowing the isolation of more stable intermediate compounds.

2. It is found that these latter consist of glyoxal, formaldehyde and formic acid.

3. The rate of reaction is accelerated by oxygen when acetylene is in excess but is slightly retarded by it when present in excess.

4. At the optimum oxygen concentration the rate is proportional to the square of the acetylene concentration, while when less oxygen is present it is proportional to a lower power of acetylene.

5. Nitrogen has a very slight retarding influence on the rate.

6. The reaction exhibits an induction period which is due to gradual accumulation of an intermediary product taking part in the chain.

7. It is pointed out that in the presence of reacting acetylene, formaldehyde reacts with oxygen many times faster than when alone.

8. The bearing of these observations on the reaction mechanism is discussed.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE ATOMIC WEIGHT OF URANIUM LEAD FROM SWEDISH KOLM

BY GREGORY PAUL BAXTER AND ALLEN DOUGLASS BLISS

RECEIVED OCTOBER 9, 1930 PUBLISHED DECEMBER 18, 1930

In connection with the work of the Committee of the National Research Council on the Measurement of Geologic Time by Atomic Disintegration, the determination of the uranium–lead ratio in the ash of Swedish kolm[1] has recently been completed. Thorium could not be detected. Since the accuracy of the age estimation is vitally dependent on the freedom of the material from lead of non-radioactive origin, the atomic weight of this lead has been compared with that of ordinary lead.

The ash of the kolm constitutes from 20 to 40% of the original, and contains a few hundredths of a per cent. of lead. In the extraction process outlined below the lead recovered amounted to 0.03% of the ash and 0.01% of the original kolm.

After various exploratory experiments the procedure finally adopted for treating the 50 odd kilograms of kolm was as follows. The material was burned in portions in electrically heated muffles of fused quartz. Practically all of the combustible portion was removed in this way. The almost insoluble ash, which yielded little lead to aqueous reagents except hvdrofluoric acid, was then heated to redness in a current of dry hydrogen chloride. Almost no lead chloride distilled during this treatment but the solution obtained by digesting the residue with hot water was found to contain the greater part of the lead, for the insoluble residue, when tested spectroscopically in an arc of pure graphite, was found to be nearly lead free. The lead was separated from the solution by double precipitation as the sulfide in ammonium acetate solution, and then was precipitated once as chromate. The total yield of lead chromate from the fifty kilograms of kolm was 7.2 g., equivalent to 4.6 g. of metal.

The outline of the further purification of this material was as follows: (1) conversion of the chromate to chloride by evaporation with hydrochloric acid; (2) conversion of chloride to nitrate by evaporation with nitric acid; (3) three crystallizations of the nitrate, once from concentrated nitric acid, twice from water; (4) conversion of the nitrate to chloride by repeated evaporation with an excess of hydrochloric acid; (5) recrystallization of the chloride, once in glass and twice in platinum;

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[1] A shale-like material reported to be an upper Cambrian sedimentary with trilobites. For further details and references as to the lead–uranium ratio, age, etc., see the reports of the Committee on the Measurement of Geological Time by Atomic Disintegration to the Division of Geology and Geography of the National Research Council.

(6) distillation of the chloride in a current of dry hydrogen chloride in a quartz tube. The product was used in Analysis K2

A second sample was obtained from the combined mother liquors of the nitrate and chloride crystallizations by evaporation with hydrochloric acid, and was crystallized twice in glass and three times in platinum. After distillation in hydrogen chloride the product was used in Analysis K1.

As soon as the first two analyses had been completed, the resulting lead nitrate solution was evaporated, freed from silver with a small amount of hydrochloric acid, and subjected to a new purification consisting of three crystallizations of the nitrate from nitric acid and four of the chloride from water, once in quartz and three times in platinum (Analysis **K3).** From the chloride mother liquors of **K3** a fourth, less pure, sample was prepared by one crystallization of the chloride in glass and one in quartz (Analysis K4).

All of the material was again combined and purified, this time by five crystallizations of the nitrate from nitric acid and five of the chloride from water, once in quartz and four times in platinum (Analysis K5).

Analysis K6 was carried out with the same material after six crystallizations of the nitrate, and six of the chloride, one of the latter being conducted in quartz and five in platinum.

Common lead chloride[2] for comparison was prepared by three crystallizations as lead nitrate, and three as lead chloride. The latter was then distilled once in a current of hydrogen chloride as described above.

To prepare the lead chloride for weighing it was fused, while contained in a weighed quartz boat in a quartz bottling apparatus, in a current of dry hydrogen chloride, and allowed to solidify in an atmosphere of pure dry nitrogen. After displacement of the nitrogen by dry air, the boat was transferred to the weighing bottle and reweighed. Solution in hot water was followed by precipitation with a weighed, very nearly equivalent amount of the purest silver,[3] and the end-point of the precipitation was determined nephelometrically in the usual way. Final observations of the end-point were taken only after a period of from three to five weeks.

Purification of reagents followed conventional lines. Especial pains were taken during the extraction of the lead from the kolm that all reagents should be lead-free.

Weighings were made by substitution, a counterpoise being employed with the weighing bottle containing the boat. Vacuum corrections of +0.000058 and −0.000031 gram were applied to each gram of lead chloride and silver, respectively.

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[2] From Coeur d'Alêne lead–silver ores.

[3] The silver used in all analyses except K3 and K4 was purified by Professor S. Ishimaru [THIS JOURNAL, 51, 1729 (1929)]. In Analyses K3 and K4 material was used prepared in the same way for this work with the assistance of Mr. J. P. Marble.

TABLE I

THE ATOMIC WEIGHT OF LEAD

	Wt. of $PbCl_2$ in vacuum, g.	Ag = 107.880 Wt. of Ag in vacuum, g.	Ag added or subtracted, g.	Corrected wt. of Ag, g.	Cl = 35.457 Ratio $PbCl_2$:2Ag	At. wt. of lead
C1	2.74332	2.12809	0.00000	2.12809	1.28910	207.222
C2	3.60741	2.79852	.00000	2.79852	1.28904	207.209
C3	3.07537	2.38552	+ .00013	2.38565	1.28911	207.224
C4	2.81471	2.18360	− .00009	2.18351	1.28908	207.218
				Average	1.28909	207.218
K1	1.61294	1.25431	+ .00247	1.25678	1.28339	205.990
K2	1.60407	1.24958	+ .00025	1.24983	1.28343	205.999
K3	2.56499	1.99848	− .00006	1.99842	1.28351	206.016
K4	1.83748	1.43153	+ .00014	1.43167	1.28345	206.003
K5	3.32075	2.58750	− .00021	2.58729	1.28349	206.011
K6	3.07451	2.39535	− .00005	2.39530	1.28356	206.027
				Average	1.28347	206.008
				Average omitting K1 and K4	1.28350	206.013

The determinations with common lead are consistent and in accord with the modern value for the atomic weight of this substance. The analytical procedure seems therefore to be satisfactory.

The atomic weight of the kolm lead seems to be close to 206.01 whether or not the two analyses with possibly less pure material, K1 and K4, are omitted. This value is surprisingly low, for the lowest value previously obtained, by Honigschmid and Horowitz, is 206.046, for lead from Morogoro pitchblende. Since Aston has found the lead isotopes to be integral with the mercury isotopes, and since these, making allowances for the presence of O^{18}, possess integral values on the basis of ordinary oxygen, the kolm lead seems to be composed almost exclusively of the isotope Pb^{206}. Compensation between isotopes of mass above and below 206 is unlikely, for there is no certain evidence of the existence of lead isotopes below 206.

The low value for the kolm lead excludes the possibility of serious contamination with common lead, which consists largely of the isotopes Pb^{207} and Pb^{208}, and is in accord with the fact that thorium has not been detected in the kolm ash. If the small excess in the atomic weight of the kolm lead over 206 is due to the isotope Pb^{207}, the proportion of this component is not far from 1%. Aston has found this isotope to be more than one-tenth as abundant as Pb^{206} in uranium lead from broggerite. If Pb^{207} is the end product of the actinium series, on the basis of Aston's result an atomic weight not less than 206.1 is to be expected for uranium lead unless the broggerite lead was badly contaminated with ordinary lead.

If actinium is not a direct product of the disintegration of U^{238}, but of an isotope, it may be that the organic process which produced the kolm exerted a selective action upon uranium isotopes, which resulted in the concentration of the isotope of mass 238. Examination of the uranium contained in the kolm might throw some light upon this question. This we propose to do.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR. MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE ATOMIC WEIGHT OF URANINITE LEAD FROM WILBERFORCE, ONTARIO, CANADA

BY GREGORY PAUL BAXTER AND ALLEN DOUGLASS BLISS

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As a check on the age determination of a specimen of uraninite occurring in Cardiff township near Wilberforce, Ontario, Canada, by means of the uranium–thorium–lead ratio the atomic weight of the lead has been determined.[1]

A selected crystal of 700 g. was broken up with a clean hammer and anvil and the fragments crushed in a carefully cleaned jaw crusher. The product was then coarsely ground in a Quaker grinding mill. This mill had been previously cleaned by passing through it a considerable quantity of marble. The marble powder was found to be free from detectable quantity of lead.

About 300 g. of the powdered uraninite was boiled with concentrated nitric acid, and the residue, which later was found to consist largely of fluorspar, was separated and washed by decantation. From the solution the lead was precipitated by adding an excess of sulfuric acid and the precipitate was washed by decantation. The lead sulfate was metathesized to the carbonate by repeated treatment with hot sodium carbonate solution, and after the lead carbonate had been washed by decantation it was dissolved in nitric acid and freed from a small amount of insoluble material.

The original insoluble residue was further boiled first with nitric acid, and again after the addition of sulfuric acid, and the whole was evaporated to the fuming point of sulfuric acid. After being washed with water the residue was extracted with hot ammonium acetate solution, and the lead was precipitated as chromate. This in turn was washed and converted to sulfate by treatment with nitric and sulfuric acids. Conversion to nitrate was accomplished as in the case of the main portion and the two portions were then combined.

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[1] For a description of geologic occurrence and analyses, by Ellsworth, Todd. Spence and Carnochan, see Exhibit A, appended to the mimeographed report of the Committee on the Measurement of Geological Time by Atomic Disintegration to the division of Geology and Geography of the National Research Council, May 3, 1900. Also *Trans. Can. Inst. Min. and Met.*, *2* (1930); *Amer. Mineralogist*, (Oct., 1930).

Since the glass dishes employed were obviously etched, owing to liberation of hydrofluoric acid from the fluorspar, in order to discover whether lead had been introduced from the dishes, they were separately heated with hydrofluoric acid solution, and the extract after evaporation was tested for lead. Since the total quantity of lead chromate recovered by treatment of three watch glasses, a beaker, flask and two porcelain evaporating dishes was only 0.0022 g., no serious contamination with common lead could have occurred during the treatment of the uraninite with acid.

The combined lead nitrate solution was evaporated to dryness to expel the excess of acid and then was recrystallized four times by solution in water and precipitation with a large quantity of concentrated nitric acid. The earlier experience of Baxter and Grover[2] showed that this treatment is adequate for removal of foreign metals. Solution of the nitrate in water was then followed by filtration through a platinum sponge crucible into a quartz dish. A considerable excess of hydrochloric acid was next added and the precipitated lead chloride was washed by decantation. Finally the chloride was recrystallized from water, once in quartz and three times in platinum.

To remove traces of silica the chloride was dried and sublimed in a current of dry hydrogen chloride in a quartz tube. It was prepared for weighing by fusion in a weighed quartz boat in a Richards bottling apparatus. Weighing of the chloride was followed by solution and precipitation with a weighed equivalent amount of the purest silver,[3] and the end-point of the precipitation was found with the assistance of the nephelometer by the addition of small amounts of dilute silver and chloride solutions.

Only two determinations were made since the original estimate of the probable atomic weight of this lead proved to be correct and the concordance of the two experiments was all that could be desired. Weighings were made by substitution and the weights of lead chloride and silver were corrected to vacuum by applying for each gram the corrections +0.000058 and −0.000031 g., respectively.

TABLE I

THE ATOMIC WEIGHT OF LEAD

	Ag = 107.880			Cl = 35.457	
Wt. of $PbCl_2$ in vacuum, g.	Wt. of Ag in vacuum, g.	Ag added, g.	Corrected wt. of Ag in vacuum, g.	Ratio $PbCl_2/2Ag$	Atomic wt. of lead
3.74779	2.91798	+0.00010	2.91808	1.28433	206.194
5.63102	4.38431	+ .00005	4.38436	1.28434	206.196
			Average	1.28434	206.195

Wells has analyzed the identical specimen of uraninite from which the lead which we have investigated was extracted and finds 53.52% of ura-

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[2] Baxter and Grover, THIS JOURNAL, 37, 1031 (1915).

[3] Purified by Professor Ishimaru for an investigation on the atomic weight of meteoric nickel, *ibid.* 51, 1729 (1929).

nium, 10.37% of thorium and 9.26% of lead. If one assumes (1) that our material is essentially free from ordinary lead, (2) that the relation of Pb^{206} to Pb^{207} found by Aston in broggerite material, 86.8 to 9.6, is the relation in which these isotopes are produced from uranium and (3) that the uranium equivalent of thorium in lead-producing power is 0.38, the average atomic weight of the lead in this specimen of uraninite may be calculated to be 206.23. The difference between this value and our experimental value is far larger than the experimental uncertainty.

With Wells' percentages and the thorium–uranium constant, 0.38, together with the experimental value of the atomic weight of the lead in this uraninite, the average atomic weight of uranium lead is found to be 206.06, while Aston's ratio of Pb^{206} to Pb^{207} gives 206.10. On this basis the ratio of Pb^{207} to Pb^{206} would be a little over half as large as that found by Aston.

The assumption of Aston's ratio of Pb^{207} to Pb^{206} in uranium lead together with Wells' percentages of uranium and thorium and the atomic weight of our specimen of uraninite lead makes it possible to calculate the Th/U constant to be 0.27, a value believed by some to be within the bounds of possibility.

The uncertainty of the assumptions makes the last three calculations of doubtful value.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COE COLLEGE]

THE ACTIVITY COEFFICIENT OF COPPER IODATE IN AQUEOUS SALT SOLUTIONS

BY BEN H. PETERSON AND EARL L. MEYERS

RECEIVED OCTOBER 15, 1930 PUBLISHED DECEMBER 18, 1930

Bronsted and La Mer[1] have reduced the Debye and Hückel equation[2] to $-\log f = 0.505\, z_1\, z_2 \sqrt{\mu}$ as a limiting law which is valid when the ions are separated to such distances that the actual volume occupied by the ions is of no effect. Considerable research has been done testing the validity of this equation by measuring the activity coefficients of slightly soluble compounds in aqueous salt solutions. La Mer and Goldman[3] have determined the activity coefficients of thallous and lanthanum iodates, and Lewis and Randall[4] have calculated them for barium iodate using the data of Harkins and Winninghoff.[5] The slight solubility of

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[1] Bronsted and La Mer, THIS JOURNAL, 46, 560–61 (1924).

[2] Debye and Huckel, *Physik. Z.*, 24, 185–342 (1923).

[3] La Mer and Goldman, THIS JOURNAL, 51, 2632–2645 (1929).

[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 375.

[5] Harkins and Winninghoff, THIS JOURNAL, 33, 1827 (1911).

these salts in pure water ($Ba(IO_3)_2$, 0.000790; $La(IO_3)_3$, 0.00089006; and $TlIO_3$, 0.001844 mole per liter), and the accuracy with which the concentration can be measured render them especially suitable for testing the limiting law. In such dilute solutions the activity coefficient of the solute may be defined by the relation[6]

$$-\log f = \log S/S_0 - \log f_0$$

in which S is the solubility of the saturating salt in the salt solution of varying concentrations, S_0 the solubility in pure water, and f_0 the activity coefficient in pure water. In such dilute solutions the value of f_0 as calculated from the limiting law may be assumed for the purpose of testing the equation. In case of most of the solvent salts used by La Mer and Goldman[3] the curve of the observed values of $-\log S/S_0$ fused into the ideal curve but a characteristic "hump" was observed in the case of potassium sulfate as the solvent salt. The theoretical significance of this positive deviation has been discussed by Gronwall, La Mer and Sandved,[7] and by La Mer and Mason.[8] In as much as the data of La Mer and Goldman[3] are for a mono- and trivalent iodate it seemed advisable to compare these deviations with those of a bivalent iodate in order to determine whether the "hump" observed by them would be in evidence and the relative magnitude of such a positive deviation.

Experimental

The salt chosen for this purpose was copper iodate. This was prepared by metathesis using purified copper sulfate and potassium iodate. Equivalent amounts of these salts were placed in solution and added dropwise to six liters of doubly distilled water kept at 60° and constantly stirred. The addition required about four hours. The precipitate was then washed several times by decantation and placed in six liters of doubly distilled water. This was kept at 60° and stirred by an electrical stirring device for several days. The salt so prepared was "sedimented" in a tall cylinder and all particles that did not settle readily were siphoned off. By several repetitions of this process it was possible to obtain a crop of crystals which appeared to be uncontaminated with small particles and should consequently be of uniform solubility. This technique is appreciably the same as used by La Mer and Goldman with lanthanum iodate. The salt when filtered and dried over calcium chloride analyzed for $Cu(IO_3)_2 \cdot H_2O$. The solvent salts were recrystallized from a high grade analyzed product, dried and analyzed for moisture and water of crystallization.

The experiments were carried out in a large especially constructed thermostat maintained at 25 * 0.02'. Ten pyrex Erlenmeyer flasks fitted with especially constructed stoppers through which a stirring rod extended were placed in the thermostat and 5 g. of the iodate added with 250 cc. of the solvent solution. The contents of the flasks were gently agitated for five days, then allowed to stand for twelve hours. These solutions were analyzed for dissolved copper iodate by dissolving 2 g. of potassium iodide in 250 cc. of water in a 500-cc. iodine flask, 5 cc. of 6 M sulfuric acid was added, then 25 cc. of

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[6] Bronsted and La Mer, THIS JOURNAL, 46,555 (1924).

[7] Gronwall, La Mer and Sandved, *Physik. Z.*, 29,358–93 (1928).

[8] La Mer and Mason, THIS JOURNAL, 49, 410–26 (1927).

the iodate solution. The contents of the flask were immediately titrated with $N/20$ sodium thiosulfate. The thiosulfate was restandardized before and after each run by exactly the same technique using 25 cc. of $N/20$ potassium iodate as the standard. Some trouble was experienced with a slow reaction between the iodide and cupric ions but the technique finally adopted allowed sufficient time to elapse between the completion of the iodate and the beginning of the cupric reaction. This was repeatedly checked using solutions of potassium iodate to which small quantities of copper sulfate had been added. In Table I is given a set of representative data illustrating the reliability of the method.

TABLE I

REPRESENTATIVE DATA

Sample	I-120, *cc*	KI, g.	H_2SO_4, *cc.*	$CuSO_4$, *cc.*	KIO_3, *cc.*	Thio, *cc*
I	200	2	5	0	25	28.40
II	200	2	5	5	25	28.37
III	200	2	5	10	25	28.37
IV	200	2	5	20	25	28.37
V	200	2	5	40	25	28.39
VI	200	2	5	100	25	28.38

Experimental Results

The solubility of copper iodate in solutions of potassium chloride, potassium sulfate, magnesium chloride and magnesium sulfate is given in Table II. The column headings are self-explanatory. The limiting law takes the form

$$-\log f = 1.01\sqrt{\mu}$$

from which the values in Column 6 are calculated. $-\log f_0$ equals 0.1063, obtained from the above equation when μ represents the ionic strength of the copper iodate in the pure water solution.

TABLE II

SOLUBILITY RELATIONS OF COPPER IODATE IN VARIOUS SOLVENTS

Solvent, Salt, KC1

Solubility, mole/liter	μ	$\sqrt{\mu}$	Log S/S_0	−Logf (obs.)	−Logf (calcd.)	A log
0.003693	0.01108	0.10526	.....	0.1063	0.1063	0.0000
.003724	.01167	.10803	0.00363	.1099	.1091	.0008
.003725	,01217	.11032	.00375	.1100	.1114	− .0014
.003825	,01647	.12833	.01525	.1215	.1296	− .0071
.003992	,02198	.14843	.03381	.1401	.1499	− .0098
.004667	.06400	.25300	.10166	.2020	.2555	− .0535
,005238	.11571	.34020	.15179	.2581	.3434	− .0853
,007689	.52306	,72320	.31849	.4248	.7302	− .3054
.009615	1.02884	1.01430	.41557	.5219	10241	− .5022
.013072	2.03922	1.42800	.54897	.6553	1 4423	− .7870
.015820	3.04746	1.74570	,63183	.7381	1 7635	−1.0254

Solvent Salt, K_2SO_4

Solubility, mole/liter	μ	$\sqrt{\mu}$	Log S/S_0	−Logf (obs.)	−Logf (calcd.)	A log
0 003693	0.01108	0 10526	.....	0 1063	0.1063	0.0000
,003785	.01285	.11340	0.01069	.1170	.1145	.0025
,003882	.01465	.12104	.02168	.1280	.1222	.0058
.004359	.02808	,16758	.07201	.1783	.1682	.0101

TABLE **II** *(Concluded)*

Solubility, mole/liter	μ	$\sqrt{\mu}$	log S/S_0	−Log f (obs.)	−Log f (calcd.)	Δ log f
0.004856	0.04457	0.21112	0.11890	0.2252	0.2131	0.0121
.006840	.17052	.41389	.26468	.3710	.4180	− .0470
.008279	.30248	.55000	.35060	.4069	.5555	− .1486
.015010	1.54503	1.24301	.60900	.7153	1.2524	− .5371
			Solvent Salt, $MgCl_2$			
0.003693	0.01108	0.10526	.....	0.1063	0.1063	0.0000
.003775	.01283	.11328	0.00954	.1158	.1144	.0014
.003821	.01446	.12025	.01480	.1211	.1214	− .0003
.004151	.02775	.16659	.05077	.1570	.1683	− .0113
.004415	.04355	.20868	.07755	.1838	.2088	− .0250
.005742	.16933	.41150	.19168	.2980	.4191	− .1211
.006446	.32354	.56880	.24191	.3482	.5745	− .2263
.009892	1.46577	1.21070	.42790	.5342	1.2222	− .6880
.011658	3.11027	1.84660	.49927	.6056	1.8645	−1.2589
.013946	4.38494	2.09401	.57709	.6834	2.1149	−1.4315
			Solvent Salt, $MgSO_4$			
0.003693	0.01108	0.10526	.....	0.1063	0.1063	0.0000
.003794	.01338	.11568	0.01172	.1180	.1168	.0012
.003845	.01554	.12463	.01752	.1238	.1258	− .0020
.004194	.03288	.18133	.05525	.1616	.1831	− .0215
.004526	.05358	,23147	.08833	.1946	.2338	− .0492
.005921	.21776	.46665	.20502	.3113	.4713	− .1600
.006225	.41867	.64705	.22676	.3331	.6535	− .3204
.011294	2.03388	1.42600	.48547	.5918	1.4403	− .8485

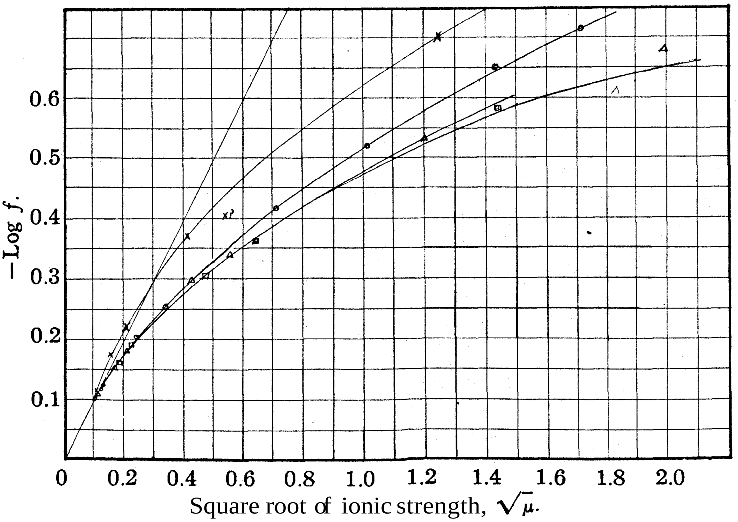

Fig. 1.—The relation of the activity coefficient, f, and the ionic strength, M, for copper iodate. The straight line is the theoretical equation, $-\log f = 1.01\sqrt{\mu}$; X, K_2SO_4; O, KCl; A, $MgCl_2$; □, $MgSO_4$.

A plot of the data is shown in Fig. 1. The line marked "limiting tangent" is the Debye and Huckel limiting law. The potassium chloride,. magnesium chloride and magnesium sulfate curves fuse fairly well into the limiting tangent but the potassium sulfate curve shows the characteristic "hump" obtained by La Mer and Goldman for lanthanum and thallous iodates. This salt also increases the solubility of the iodate more than the others. The general deviation from the theoretical lies somewhere between the deviations of the uni- and trivalent iodates mentioned.

Summary

The activity coefficients of copper iodate have been measured by the solubility method in aqueous solutions of the chlorides and sulfates of potassium and magnesium. The solubility of copper iodate is **0.003693** mole per liter at 25°.

CEDAR RAPIDS, IOWA

NOTES

The Detection of Cobalt as Cesium Cobaltinitrites.—The oxidation of cobaltous ion in acid solution by a concentrated solution of potassium nitrite and its precipitation as the yellow cobaltinitrite are well known in the conventional scheme of analysis. The potassium salt, however, has an appreciable solubility and for low concentrations of cobaltous ion has the undesirable property of precipitating slowly. The corresponding cesium salt, on the other hand, is more insoluble and precipitates and settles much more rapidly. At 17° one cubic centimeter of saturated solution contains approximately 0.05 mg. of the cesium salt.[1] In terms of cobaltous ion the concentration is considerably less and hence serves as a very delicate test for this ion.

Procedure.—The mixture of cobalt and nickel sulfides, from the usual procedure, is dissolved in aqua regia and evaporated just to dryness. The residue is dissolved in one or two cc. of 6 M acetic acid. To this solution 2 cc. of 6 *M* sodium nitrite and 0.5 cc. of 0.5 *M* cesium nitrate (or 0.25 *M* cesium sulfate suggested as a reagent for aluminum)[2] are added and the yellow $Cs_2NaCo(NO_2)_6$ precipitates.

The following table illustrates the delicacy and rapidity of the test

Concn. of cobaltous ion, mg. per cc..	0.5 and greater	0.2–0.5	0.05
Time for precipitation, min..	Instantaneous	0.5	2

The sensitivity of the test may be increased by substituting potassium nitrite for the corresponding sodium salt in the previously described pro-

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[1] Rosenbladt, Ber., 19, 2531 (1886).

[2] Yagoda and Partridge, THIS JOURNAL, 52,3579 (1930).

cedure. If this is done, a solution of cobaltous ion containing 0.01 mg. per cc. will yield a yellow precipitate (probably $Cs_2KCo(NO_2)_6$) in about three minutes.[3]

Considerable quantities of iron, manganese or nickel do not interfere with the cobaltinitrite precipitation.

The authors acknowledge with thanks the kind cooperation of the Maywood Chemical Works.

CONTRIBUTION FROM THE
CHEMICAL LABORATORIES OF THE
WASHINGTON SQUARE COLLEGE OF
NEW YORK UNIVERSITY
NEW YORK, N. Y.

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HERMAN YAGODA
H. M. PARTRIDGE

Inorganic Lubricants. IV. Lubricants for Temperatures Above and Below Normal. A. For Temperatures Above Normal.—Aqueous metaphosphate and metaphosphoric acid solutions yield clear, viscous lubricants capable of operating up to 120° and by selection to 160°, the operating range of temperature (Op. r.) over which any particular solution has satisfactory lubricating properties depending upon the temperature at which boiling of that solution is stopped (T. b.) Typical examples are listed in Table I.

TABLE I

BOILING TEMPERATURES AND APPROXIMATE OPERATING TEMPERATURE RANGES FOR VARIOUS METAPHOSPHATE SOLUTIONS

A. Aqueous solutions of metaphosphoric acid containing approximately 20% of added orthophosphoric acid

T. b., °C.	140	150	165	185	205
Op. r., °C.	25–30	40–60	45–70	55–75	65–80
T. b., °C.	230	260	300	350	
Op. r., °C.	70–85	80–95	105–120	Fumes	

B. Solutions of sodium metaphosphate

T. b., °C.	107 [a]	110 [a]	115	120
Op. r., °C.	25+	50–65	60–85	65–90

C. Solutions of sodium metaphosphate containing approximately 20% of borax and 10% of added orthophosphoric acid

T. b, °C.	110	115	122 [a]	118	125
Op. r., °C.	25+	60–80	70–90	50–80	90–160

[a] The solution was then diluted and again boiled down to avoid crystallization at the operating temperature range.

These lubricants in their respective operating ranges have properties quite similar to those of the phosphoric acid and metaphosphate lubricants

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[3] Cf. Noyes and Bray, "A System of Qualitative Analysis for the Rare Elements." The Macmillan Company, New York, 1927, p. 202.

previously described.[1a] In general, the operating range rises during their protracted use at elevated temperatures because of further slow dehydration.

A variety of salts melted in their water of crystallization and, at higher temperatures, certain anhydrous salts yield liquids which, when mixed with sufficient quantities of finely powdered, non-reacting, stable solids to form stiff, creamy pastes, afford lubricants similar to those obtained by mixing such solids with aqueous solutions of deliquescent substances,[1b] but having operating ranges up to their reaction or decomposition temperatures.

TABLE II

OPERATING RANGES OF MIXTURES OF FUSED SALTS WITH FINELY DIVIDED SOLIDS

Subs.	M. p., °C.	Mixed with powdered	Op. r.. °C.	Remarks
$Ca(NO_3)_2 \cdot 4H_2O$	42	Graphite	45–120	Supercools
$Na_2B_2O_4 \cdot 2H_2O$	57	Graphite	55–110	Supercools
$Na_2S_2O_3 \cdot 5H_2O$	48	Graphite	70–110	SO_2 evolved
$Mg(NO_3)_2 \cdot 6H_2O$	90	Kaolin	110–200	
KSCN	172	Kaolin	175–320	
KNO_3	337	Kaolin	340–360	Decomposes above 360"

A mixture of equal parts by weight of crystallized calcium nitrate and potassium nitrate when heated to 120° and stirred until a clear solution of calcium nitrate in the potassium salt was thus obtained yielded a liquid that when mixed with kaolin gave a series of lubricants of increasing temperature ranges depending on the temperatures at which boiling the liquid was stopped.

TABLE III

BOILING TEMPERATURES OF MIXED CALCIUM AND POTASSIUM NITRATES AND OPERATING RANGES OF LUBRICANTS CONTAINING KAOLIN

T. b., °C.	150	185	200	225
Op. r., °C.	140–160	150–180	155–190	160–220
T. b., °C.	260	300	340	
Op. r., °C.	170–260	170–300	170–340	

It appears to be possible, therefore, to select a mixture of fused salt and non-reacting solid to melt under almost any required condition of high temperature inorganic lubrication. Mixtures of this kind are also useful as reversibly thermoplastic lutes.

B. Lubricants Operating at Temperatures Below Normal.—The same classes of materials in different concentrations also yield lubricants capable of operating at subnormal temperatures. Thus aqueous solutions of metaphosphoric acid boiling at the stated temperatures give approximately the following ranges of temperature for satisfactory lubrication.

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[1] Boughton, THIS JOURNAL, 52, (a) 2813; (b) 4335 (1930).

TABLE IV

BOILING TEMPERATURES AND OPERATING RANGES FOR A SOLUTION OF METAPHOSPHORIC ACID

T. b., °C.	105	110	115	120
Op. r., °C.	−75 to −65	−60 to −50	−40 to −30	−15 to 0

Sodium metaphosphate solutions have more limited usefulness as low temperature lubricants. Those boiling at 104–106° have an operating range of −25 to 0°. More dilute solutions freeze when cooled to a temperature of a few degrees below zero.

Lubricating cream mixtures of salt solutions and finely divided solids may be prepared in the usual way and can then be used at temperatures down to approximately the freezing points of the respective solutions. Thus, a 35% solution of calcium chloride mixed with kaolin may be used as a lubricating paste to temperatures as low as −20°.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

WILLIS A. BOUGHTON

RECEIVED OCTOBER 21, 1930
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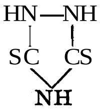
[CONTRIBUTION FROM THE ORGANIC CHEMISTRY DEPARTMENT, INDIAN INSTITUTE OF SCIENCE]

CONSTITUTION OF THE SO-CALLED DITHIOURAZOLE OF MARTIN FREUND. IV. ISOMERISM OF HYDRAZODITHIODICARBONAMIDES, IMINO-THIOL-THIOBIAZOLES AND IMINO-THIOBIAZOLONES

BY SHAHA L. JANNIAH AND P. C. GUHA

RECEIVED MAY 24, 1930 PUBLISHED DECEMBER 18, 1930

The ring-closing action of various reagents upon hydrazodithiodicarbonamides and their alkyl and aryl substituted derivatives has been studied by a number of workers, *viz.*, by Freund, Busch, Arndt, Fromm, Guha and their collaborators beginning from the year 1893, and all the possible four types of triazoles and thio-biazole compounds, I, II, III and IV, obtainable from the hydrazides, have been isolated.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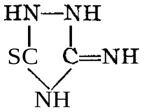
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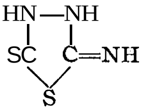
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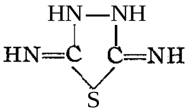
IV

A careful survey of the literature reveals the fact that various authors attribute different melting points to one and the same substance. As an example, to imino-thio-tetrahydro-4,1,2-thiodiazole, Freund[1] gives the

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[1] Freund, Ber.. 28, 946 (1895).

melting point 243°; Guha[2] attributes three different melting points, *viz.*, 244, 233 and 224°, and Fromm[3] gives 228–235°. So it appears that the various investigators did not take sufficient care to define exactly the conditions under which they worked, so that the attempted repetitions were hindered by a lack of exact knowledge of the experimental conditions employed by earlier investigators. The present work was, therefore, undertaken with a view to defining more clearly the various factors which are concerned in the formation of each of the types of compounds.

In this paper, which forms the beginning of a series of investigations, it is proposed to deal with hydrazodithiodicarbonamides and the imino-thiolthiobiazoles.

Hydrochloric acid being rather an important ring-closing agent, its behavior on the hydrazides has now been very systematically studied and the utmost care has been taken to learn the influence of two important factors, *viz.*, the concentration of the acid and duration of treatment. After several trials 2 *N* acid, 5 N acid, strong (d 1.16) acid and concentrated (*d* 1.19) hydrochloric acid have been found to be suitable.

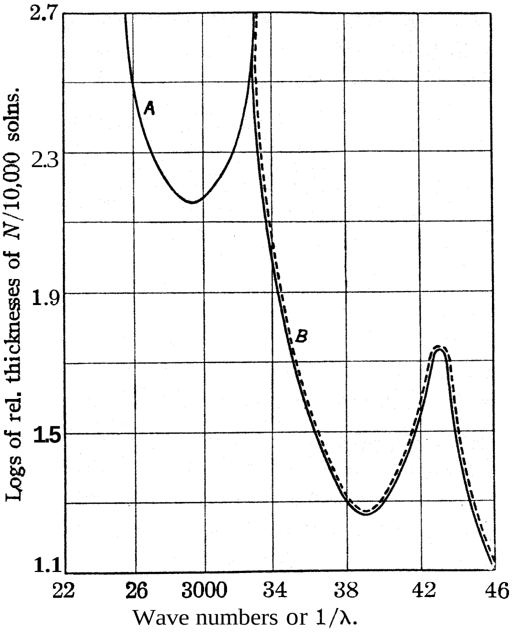

Fig. 1.—A, $NH{=}C(SH)NHNHC(SH){=}NH$, m. p 203°; B, $NH_2CSNHNHC(SH){=}NH$, m. p. 223°.

Hydrazo-dithio-dicarbonamide (m. p. 223°) on being boiled with dilute hydrochloric acid for a short time gave instead of a ring compound another hydrazide having the same chemical composition, $C_2H_6N_4S_2$, yielding derivatives (acetyl, methyl ether) identical with those of the parent hydrazide but differing in the melting point (m. p. 203°), suggesting thereby that the new compound is an isomer. While the hydrazide (m. p. 223°) has given only one absorption band (B) in Fig. 1, the isomer has given two bands (Curve A); and when the lower-melting variety was reconverted to the higher one, only one band, identical with that of the parent hydrazide, was obtained.

In these substances, we are dealing with a simple case of tautomerism,

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[2] Guha, This Journal, **44,** 1502–1517 **(1922).**

[3] Fromm. Ann.. 426,313 **(1922).**

for they do not contain anything benzenoid in structure, which is always accompanied by absorption bands. From a consideration of the investigation on the ultraviolet absorption spectra of some enol–keto tautomerides by Baly and Desch,[4] the conclusion to be drawn from these results can only be that the 223° variety exists in the monothiol form, whilst the new variety exists in the dithiol form, thus

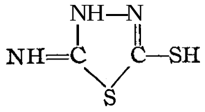
$NH_2CSNHNHC(SH){=}NH$ (m. p. 223°)
$NH{=}(HS)CNHNHC(SH){=}NH$ (m. p. 203°)

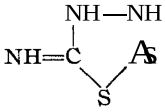
In the former, the hydrogen atom of only one of the (—$CSNH_2$) groups can oscillate to give rise to the tautomeric thiolimino form —C(SH)=NH, accounting for one absorption band; and in the latter, the hydrogen atoms of both such groups can oscillate, as the result of which it gives two bands.

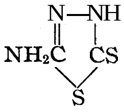
Both the hydrazides on being boiled with dilute hydrochloric acid for a long time, or with concentrated acid for a short time, yielded a ring compound of composition $C_2H_3N_3S_2$ melting at 234°.[3] In all chemical behavior it was identical with Freund's compound melting at 244–245°.

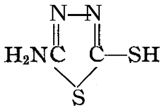
The acetyl derivative (m. p. 303°) of the above compound (m. p. 234°) when hydrolyzed with hydrochloric acid, gave back a substance possessing the same chemical composition, *viz.*, $C_2H_3N_3S_2$, but melting at 245°. This compound was obtained also by boiling the hydrazodithiodicarbonamide with concentrated hydrochloric acid (sp. gr. 1.19) for about half an hour. It does not respond to the tests of the amino group and behaves chemically identical with the parent substance (m. p. 234°).

It has also been observed that the higher-melting variety, obtained by either of the methods as stated above, on standing for several weeks is converted into the lower-melting variety 234°. The question naturally arises whether it is possible to explain this difference by any other tautomeric formula.









Of these the third and the fourth can easily be discarded owing to the fact that the substances do not respond to any test for the amino group. As regards the first and the second, it is very doubtful whether any such tautomeric compounds can exist at all as separate individuals.

Chemical methods proving of no avail in finding out the real cause of the difference, it was thought advisable to examine and compare the absorption spectra of these two compounds. It will be noticed that the difference existing among all the four suggested formulas is only due to a labile hydrogen atom. If this is really the case, then there ought to have been only

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[4] **Baly and Desch,** *J. Chem. Soc.*, **85, 1033–1036 (1904).**

a slight difference either in the persistence of the band or in the number of bands obtained from the two varieties. It has been actually found that the lower-melting variety gives a band between the wave numbers 3400 and 4200 in Fig. 2, while the higher-melting variety gives the band in the region between 2500 and 3600. This means that there has been a shift in the curve while passing from one variety to the other isomeric form. This eliminates the possibility of the difference being due only to a labile hydrogen atom.

It is necessary here to describe another case of isomerism observed by us. Martin Freund, by treating hydrazomonothio-dicarbonamide with strong hydrochloric acid, obtained a compound (m. p. 177°) which he called monothiourazole.[5] The same hydrazide on being treated with acetic anhydride[6] was found to give a basic compound possessing the same chemical composition as that of Freund, but melting at 235°. The latter compound differs from the former in that it forms derivatives with aldehydes, isocyanates and mustard oils, proving conclusively the presence of an amino group.

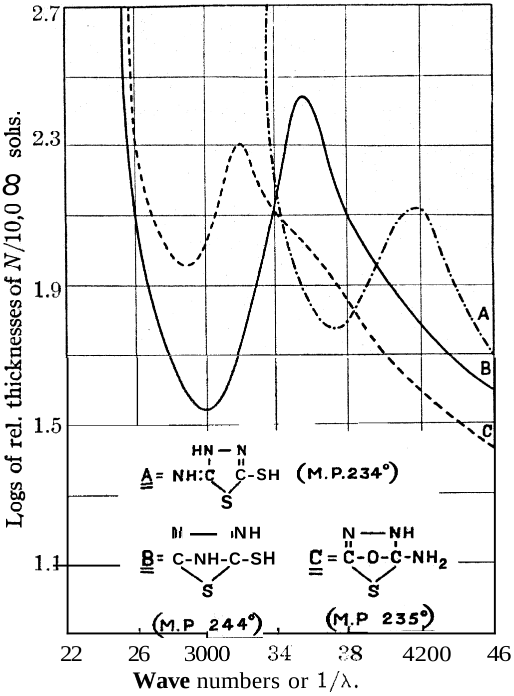
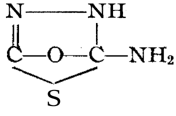


Fig. 2.

In view of these observations the new isomeric compound can only be represented by an endo formula, *viz.*, 3-amino-3,5-endoxy-2,3-dihydro-4, 1,2-thiodiazole (X). Freund's compound possesses none of these properties, and is feebly acidic in character, due evidently to the presence of an (—NH—CO—) group. So, to account for the pronounced basic nature of the new compound and to explain the mechanism of conversion of Freund's monothiourazole to that obtained by Guha, it is proposed to attribute an endo structure to the latter, and the changes involved in the transformation can be represented thus



X

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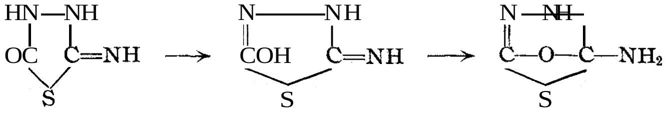
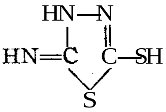
[5] Proved by Arndt to be imino-thiobiazolone, Ber., 55,341 (1922).

[6] Guha, This Journal, 45,1038 (1923).

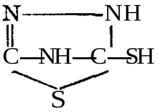


For purposes of analogy the curve of the endoxy-aminothiodiazole is also given, and it will be noticed that the curve of the 245° variety occupies almost the same region.

From all that has been said so far, and also to explain the difference between the two forms, melting at 234 and 245°, on a structural basis, as distinct from a basis of tautomerism, as established by absorption spectra curves, it is proposed that an imino-thio-tetrahydro-thio-diazole **(A)** structure be attributed to the lower-melting variety and an endo structure (*viz.*, 3-thiol-3,5-endo-imino-2,3-dihydro-4,1,2-thiodiazole) to the higher-melting variety.



(A, m. p. 234°)



(B, m. p. 245")

Similar experiments have also been made with the substituted hydrazides. The results have corroborated the observations made in this paper and will be communicated shortly.

Experimental

Isomeric **Hydrazodithiodicarbonamide.**—Five grams of hydrazo-dithio-dicarbonamide, m. p. 223° (prepared according to the method of Freund[1]), was heated with 100 cc. of 2 *N* hydrochloric acid over a small flame until dissolved and the solution kept boiling for just ten minutes. The solution was then allowed to cool slowly, when colorless tiny needles separated. These were filtered, washed with a little water and recrystallized from hot water. The colorless crystalline needles thus obtained melted sharply at 203°. The melting point remained unchanged on repeated crystallizations; yield almost quantitative. This substance was found to be soluble in alkali more readily than the parent hydrazide; but both the hydrazides gave identical compounds when treated with dimethyl sulfate (m. p. 174°), and even the analytical values were the same. (The absorption spectra of the two have been studied in aqueous solutions.)

Anal. Calcd. for $C_2H_6N_4S_2$: N, 37.33; S, 42.66. Found: N, 37.2; S, 43.0.

Interconversion of the Two **Hydrazides.**—Two grams of hydrazodithiodicarbonamide (m. p. 223°), was dissolved in a little excess of 2 N sodium hydroxide and the clear solution kept aside in a closed flask for about twenty-four hours. The solution was then acidified with dilute hydrochloric acid, when a thick colorless solid was thrown down. This solid was filtered, washed and crystallized from hot water, when colorless tiny needles were obtained, melting sharply at 203°. This was proved by mixed melting point to be identical with the isomeric hydrazide obtained previously. The yield was almost quantitative except for a little loss during crystallization.

Two grams of the hydrazide (m. p. 203°) was placed in a glass dish, covered with a watch glass, in an air-oven at 120° for about four hours, when the hydrazide was found to melt at 223°. The higher-melting variety thus obtained showed no change in the melting point on repeated crystallization and was proved to be identical with the parent hydrazide (m. p. 223") by taking the mixed melting point. The absorption spectra of the 223° variety as obtained by conversion were found to be identical with that of the parent hydrazide.

Imino-thiol-dihydro-thiobiazole.—Two grams of hydrazodithiodicarbonamide (m. p. 223°) or its isomer (m. p. 203°) was boiled with 25 cc. of concd. hydrochloric acid (d 1.19) for about ten minutes. The crystalline solid obtained from the clear solution on cooling was carefully washed and recrystallized from hot water (m. p. 234°).

When the experiment was repeated with 2 N hydrochloric acid, about 60 cc. of the dilute acid was required to dissolve 3 g of the hydrazide on heating, and the solution had to be kept boiling for half an hour. The imino-thiol-dihydrothiobiazole thus obtained crystallized as very pale yellow needles, melting sharply at 234°, the yield being about 1.4 g. from 3 g. of hydrazide. It dissolves in cold dilute sodium hydroxide solution, and with iodine it gives the disulfide (m. p. 240°); with methyl sulfate it gives the thiomethyl ether (m. p. 178°); with acetic anhydride, the acetyl derivative (m. p. 303°).

Anal. Calcd. for $C_2H_3N_3S_2$: N, 31.6; S, 48.1. Found: N, 31.8; S, 47.8.

Endo-imino-thiol-thiobiazole.—Three grams of imino-thiol-dihydro-thiobiazole (m. p. 234") was heated with 20 cc. of concentrated hydrochloric acid (d 1.19) to boiling for about ten minutes and the solution was allowed to cool. Dull yellow prismatic crystals were found to separate out from the solution gradually, and were filtered, washed and recrystallized from hot water; m. p. 244°; yield, 1.2 g.

Two normal acids failed to give the endo compound (m. p. 244°) even when the solution was boiled for more than an hour, but 5 N hydrochloric acid was found to be better than concentrated acid, as it gave greater yield. The actual yield of the endo compound from 3 g. of the parent thiobiazole was 1.8 g. as compared with 1.2 g. with concentrated acid

Starting with hydrazodithiodicarbonamide (m. p. 233°) or its isomer (m. p. 203°), 5 g. of the hydrazide was heated with 40 cc. of 5 *N* hydrochloric acid until dissolved. The solution was kept boiling over a small flame for a quarter of an hour and then cooled. The solid obtained was filtered, washed and crystallized from hot water, m. p. 244°; it was found to be identical with that obtained from imino-thiobiazole (and behaving chemically identically with the "so-called 'dithio-urazole' " of Martin Freund).[1] 5 N hydrochloric acid was employed in preference to concentrated acid for good yields; yield, 3.2 g.

The substance gave with methyl sulfate the methyl ether, m. p. 178°, and the acetyl derivative, m. p. 303°, both identical with those of imino-thiol-dihydro-thiobiazole.

Acetyl Derivative of Imino-thiol-dihydro-thiobiazole.—Two and one-half grams of the thiobiazole was heated gently with 15 cc. of acetic anhydride until dissolved. The brownish-yellow solution obtained was heated to boiling and kept at that temperature for about twenty minutes. The clear solution was poured into about 100 cc. of water and when thoroughly stirred by a glass rod, a yellow solid separated, which was filtered, washed with water and crystallized from very dilute acetic acid. The pale yellow needles thus obtained melted at 303° to a dark brown liquid; yield, 1.4 g.

Hydrolysis.—The acetyl compound was boiled gently with 2 N hydrochloric acid until very little acetic acid was present in the vapors. The insoluble solid which separated on slight cooling was filtered off from the mother liquor, washed and crystallized from boiling water. The crystalline needles so obtained melted sharply at 243–244°, identical with the endo-imino-thiol-thiobiazole.[7]

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[7] The endo-imino-thiol-thiobiazole when treated similarly with acetic anhydride gave the same acetyl derivative, m. p. 303°, which on hydrolysis gave back the endo compound.

Summary

1. Hydrazodithiodicarbonamide has been found to tautomerize into the thiol-imino form under experimental conditions which have been determined, and the interconvertibility of the two forms established.

2. Imino-thiol-thiobiazole has been isolated as an intermediate compound during the formation of Freund's "Dithio-urazole"—now shown to be endo-imino-thiol-thiobiazole; the latter has been found to be formed either by the prolonged action of hydrochloric acid on the hydrazide or the imino-thiol-thiobiazole, or by acetic anhydride treatment on the thiobiazole with subsequent deacetylation.

3. Similar cases of isomerism have been observed with the alkyl and aryl substituted mono- and dithio-hydrazides.

BANGALORE, INDIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE COLLEGE OF WASHINGTON]

SOME HALOGEN DERIVATIVES OF ACYL AND ALKYL RESORCINOLS

BY C. M. BREWSTER AND J. C. HARRIS[1]

RECEIVED JUNE 19, 1930 PUBLISHED DECEMBER 18, 1930

Since the acyl and alkyl resorcinols have been given much attention by investigators recently, due to their germicidal and other interesting properties, we have undertaken to prepare and study certain halogen derivatives of these compounds, and also to improve the methods of preparation of the intermediate compounds already reported by others.

The acyl groups were introduced into the resorcinol nucleus by condensing the latter with the desired fatty acid in the presence of fused zinc chloride, a method proved to be very satisfactory for this purpose by Nencki[2] and others. The ketones were prepared without difficulty, and increased yields obtained by varying the conditions of temperature, concentration and time, as shown in the tables in the dissertation.[3] These acyl compounds were then reduced according to Clemmensen's method,[4] which employs amalgamated zinc with hydrochloric acid as reducing agent. The alkyl compounds obtained by reduction were halogenated in various solvents and in the presence of carriers.

The same halogenated alkyl resorcinol was obtained whether the halogenated ketone was reduced or the ketone reduced before halogenation. For example, dibromo-ethylresorcinol was prepared as follows.

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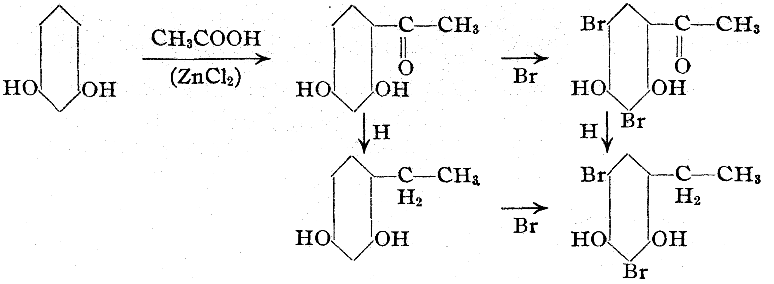
[1] This paper is an abstract of part of a thesis presented by J. C. Harris in partial fulfilment of the requirements for the degree of Master of Science.

[2] Nencki and Schmid, J. *prakt.* **Chem.,** 23, 546 (1881).

[3] Dissertation, by J. C. Harris, 1930.

[4] Clemmensen, Ber., 46, 1837 (1913).



Von Pechmann and Duisberg[5] established the position of the acetyl group when they fused β-methylembelliferone with potassium hydroxide and obtained resacetophenone. Dahse[6] determined the position of the bromine atoms in the ketone by oxidation with chromic acid and obtained a dibromo-dihydroxybenzoic acid which was identical with that formed by bromination of β-resorcylic acid. The reduction of the dibromo ketone would definitely place this compound as 2,4-dihydroxy-3,5-dibromo-ethylresorcinol.

The corresponding dichloro-ethylresorcinol was prepared by reduction of the chlorinated ketone, but we were unable to isolate the same compound when ethylresorcinol was chlorinated, although it was evident that a similar reaction had taken place. The solubility of dichloro-ethylresorcinol in water is appreciably greater than that of the dibromo-ethylresorcinol, and we could not find an extraction agent which would bring about a clear separation and yet remain immiscible with the original solvent.

On bromination of resacetophenone in acetic acid with iodine as carrier, a tetrabromo derivative was obtained. On reduction by Clemmensen's reagent, the tetrabromo derivative gave 2,4-dihydroxy-3 5-dibromo-ethylresorcinol, indicating that two of the bromine atoms are in the nucleus and two in the methyl group of the side chain.

The halogenated acyl resorcinols gave a wine-red color to an aqueous solution of ferric chloride, while the corresponding alkyl compounds gave merely a slight yellowish-green coloration. The melting points for the halogen derivatives are considerably higher than for the non-halogenated ketones, but show the usual decrease with lengthening of the side chain. Since there are two bromine atoms in the side chain pf the tetrabromoresacetophenone, their introduction reduces the melting point. Inasmuch as the melting point of tribromopropionylresorcinol is higher than that of the dibromo compound it is possible that the third bromine atom of the former may be in the benzene nucleus.

We were unable to prepare tribromoresacetophenone, reported by Segalle[7] as produced by passing an excess of bromine into an acetic acid

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[5] Von Pechmann and Duisberg, *Ber.*, **16**, 2121 (1883).

[6] Dahse, *ibid.*, 41, 1621 (1908).

[7] Segalle, *Monatsh.*, **17**, 315 (1896).

solution of the ketone. Numerous trials with different proportions and in different solvents, varying also the temperature and time, resulted in forming the dibromo compound, or in the presence of iodine as carrier, the tetrabromo derivative. However, when propionylresorcinol was brominated in glacial acetic acid, tribromopropionylresorcinol was obtained, also when iodine was used as carrier.

Halogenation products of propylresorcinol and butylresorcinol were prepared by the reduction method of Clemmensen, and the color change when tested with ferric chloride indicated complete reduction, but samples were oils of which we did not have a sufficient quantity for purification.

In the preparation of butyrylresorcinol, when the condensation was permitted to continue at boiling temperature for several minutes, the final purification gave two products: one the normal product melting at 69–70°, and the second a compound melting sharply at 111–112°, composed of clear colorless prism-shaped crystals. Several analyses were made of different trial samples but no conclusions can be reached as to its constitution until more work is done on the compound.

We are investigating further the halogen derivatives of other members of the resorcinol series, with acyl, alkyl and aryl side chains. We have also made a number of similar derivatives of hydroquinone and of the naphthols, and are continuing their study in this Laboratory.

Experimental Part

ω-Dibromo-3,5-dibromo-2,4-dihydroxyacetophenone.—Bromination took place in a hot glacial acetic acid solution of resacetophenone, using several crystals of iodine as carrier. On dilution with water, yellow crystals separated and were purified by crystallization from acetic acid and from alcohol. The characteristic sheaves of yellow platelets melt sharply at 110–110.5°.

Anal. Calcd. for $C_8H_4O_3Br_4$: Br, 68.35. Found: Br, 68.08, 68.42.

The compound is readily soluble in alcohol, benzene, ether, chloroform and acetic acid, difficultly soluble in petroleum ether and in boiling water. With ferric chloride a wine-red color is produced, as with other brominated ketones. On reduction tetrabromoresacetophenone gave 3,5-dibromo-2,4-dihydroxy-1-ethylbenzene, indicating that two of the bromine atoms of the tetrabromo derivative were in the methyl group of the side chain.

Dichloro-2,4-dihydroxyacetophenone was prepared by direct chlorination of resacetophenone in a variety of solvents and at different temperatures; the best yield (78%) was obtained when using 80% acetic acid as solvent, and the solution was heated to 80° at the beginning of the chlorine addition. Segalle[7] also used acetic acid in preparing the compound. The glistening white needles melt at 195–196°. They are insoluble in water, slightly soluble in chloroform, carbon disulfide, and petroleum ether, readily soluble in alcohol, benzene and acetic acid.

2,4-Dihydroxypropiophenone.—Propionic acid distilling between 135–145° was used in numerous trials, and most satisfactory results were obtained by dissolving 80 g. of fused zinc chloride in 80 g. of propionic acid, and adding 50 g. of resorcinol to the hot solution. The mixture was heated under reflux to an intense bubbling of the solution, which occurred between 160–165°. The solution was then allowed to cool slowly, and on the following day was warmed sufficiently to permit it to be poured into a water and ice mixture acidified with hydrochloric acid. The dark brown oil solidified on standing, and the product was purified by dissolving in alcohol and refluxing the solution with animal charcoal. Bright yellow needles separated, m. p. 96°, which were readily soluble in alcohol, benzene, ether and acetic acid, but difficultly soluble in carbon tetrachloride, chloroform, petroleum ether and water. A yield of 73% was obtained, which is lower than that reported by others[8] who used a larger proportion of acid, but the above method is more economical as technical propionic acid can be used. The oxime was prepared as bright yellow needles, m. p. 186–187°.

3,5-Dibromo-2,4-dihydroxypropiophenone.—Gnagy[9] prepared this compound by slow addition of an acetic acid solution of bromine to the ketone dissolved in acetic acid. We tried carbon disulfide as well as acetic acid as solvent, but obtained the best yield (51%) by use of 80% acetic acid, adding bromine slowly through a dropping funnel. The mixture was allowed to stand for a day, filtered, the filtrate diluted with water and allowed to stand two to four hours for crystal formation. The crystals were dissolved in alcohol, refluxed with animal charcoal and recrystallized by addition of water; m. p. 151–152°; white needles, difficultly soluble in petroleum ether, insoluble in water, but readily soluble in other solvents.

Tribromo-2,4-dihydroxypropiophenone.—The ketone, dissolved in glacial acetic acid, was treated with two and one-half times the amount of bromine theoretically required for the dibromo compound. The solution was heated to 80° before adding the bromine. On cooling, an equal volume of water was added and the crystals were filtered, washed and dried. Repeated crystallization from alcohol gave yellow flaky crystals, m. p. 157–158°, which may be dissolved with difficultly in hot water or petroleum ether, but are readily soluble in other solvents.

Anal. Calcd. for $C_9H_7O_3Br_3$: Br, 59.37. Found: Br, 59.15, 59.49.

Dichloro-2,4-dihydroxypropiophenone.—The ketone was dissolved in 80% acetic acid and chlorine was passed through until no further change was observed. A mass of white needle-like crystals separated, and dilution with water gave more of the same compound, which was recrystallized from acetic acid and water. The product was washed, dried and finally crystallized repeatedly from benzene giving white needles, m. p. 146–147°, very slightly soluble in petroleum ether, insoluble in water, but readily soluble in alcohol, benzene and other solvents.

Anal. Calcd. for $C_9H_8O_3Cl_2$: Cl, 30.18. Found: Cl, 29.97, 29.96.

2,4-Dihydroxybutyrophenone.—Sixty grams of technical butyric acid (b. p. 153–163") and 50 g. of fused zinc chloride were refluxed and when dissolved 30 g. of resorcinol was added. The mixture was heated to an intense bubbling, which occurred at about 165°. The dark brown viscous product was allowed to cool slowly until the next day, then warmed and poured into an acidified mixture of ice and water. The ketone was washed free of zinc chloride, dried and distilled repeatedly under diminished pressure, giving a light yellow oil. The product was crystallized from a mixture of equal parts of chloroform and benzene, m. p. 68–70". Johnson and Lane[8] purified the ketone by distillation under diminished pressure and crystallization from a mixture of three parts of carbon tetrachloride and one part of benzene

Gnagy[9] dissolved the oil in aqueous sodium hydroxide, refluxed repeatedly with animal charcoal and precipitated with hydrochloric acid.

Second Product.—In repeating the above process, but maintaining the mixture at the boiling temperature of 165" for two to five minutes before cooling, a different

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[8] Johnson and Lane, THIS JOURNAL, 43, 357 (1921).

[9] Gnagy, *ibid.*, 45, 807 (1923).

substance was obtained. The condensation product was purified as above, but the crystallization from chloroform and benzene gave about 20% of clear colorless crystals, m. p. 111–112°, the rest being the normal compound with melting point of 68–70'. The new compound crystallized in large clear prisms and appeared to be pure, but analyses showed less carbon and hydrogen than found in the normal compound. Unfortunately not enough of the compound was available to make derivatives for further study. We prepared the oxime of the normal compound (m. p. 68–70"), obtaining pale yellow needles, m. p. 188–189°.

3,5-Dibromo-2,4-dihydroxybutyrophenone.—Direct bromination of the ketone in 80% acetic acid solution, as employed by Gnagy, gave satisfactory results, though the yield was low. A yield of 10% was obtained when 15 g. of the ketone was brominated with 30 g. of bromine, 100 g. of 80% acetic acid being used as solvent. The compound was much more difficult to purify than the halogenated propionyl or acetyl resorcinol. It was necessary to reflux the solution repeatedly with animal charcoal, and finally to crystallize by fractional crystallization from alcohol and water. The crystals melt at 108–109°. The compound can be reduced to the alkyl form.

Dichloro-2,4-dihydroxybutyrophenone.—Twenty grams of butyrylresorcinol was dissolved in 100 g. of 80% acetic acid and chlorine passed through in excess. On dilution white crystals separated, which were refluxed in alcoholic solution with animal charcoal, and finally crystallized from benzene. The white needles (yield, 21%) were very slightly soluble in petroleum ether and in water, but readily soluble in alcohol, benzene or carbon tetrachloride. The melting point was 110.5–111°.

Anal. Calcd. for $C_{10}H_{10}O_3Cl_2$: Cl, 28.48. Found: Cl, 28.80, 28.76, 28.96.

2,4-Dihydroxy-1-ethylbenzene.—Resacetophenone was reduced by the Clemmensen method.[10] A yield of 82% was obtained as follows. Mossy zinc was amalgamated by covering with a 5% solution of mercuric chloride for one hour, then the liquid was drained off and the zinc used immediately without washing. Two hundred grams of the amalgamated zinc was placed in a flask, 50 g. of the ketone added, and 300 cc. of 20% hydrochloric acid gradually poured in to maintain steady evolution of hydrogen while the mixture was gently boiled. When a drop of the liquid gave no red color test with aqueous ferric chloride, which in this trial required about three hours, the solution was decanted, saturated with sodium chloride, cooled and extracted with ether. This general procedure was followed in all reductions and gave much better yields than the use of sodium amalgam or other reducing agents tried. When crystallized from benzene, the pale yellow crystals melt sharply at 97–98°, as reported by Clemrnensen, and also by Johnson and Hodge.[11]

3,5-Dibromo-2,4-dihydroxy-1-ethylbenzene. Reduction Method.—Dibromoresacetophenone was reduced by Clemmensen's method until the ferric chloride test showed complete reduction. The warm suspension was saturated with salt, cooled and extracted with ether. On evaporation of the ether the oily residue was dissolved in alcohol and refluxed repeatedly with animal charcoal. On cooling the diluted alcoholic solution silky crystals slowly separated. The long silky needles when first filtered were transparent, but became opaque when dried. They melted sharply at 74°.

Anal. Calcd. for $C_8H_8O_2Br_2$: Br, 54.01. Found: Br, 53.93, 54.21.

Bromination Method.—Ethylresorcinol was dissolved in a variety of solvents and the calculated amount of bromine for the dibromo product was added. The solvents tried were glacial acetic acid, 80% acetic acid, ether, carbon disulfide, chloroform and carbon tetrachloride; ether gave the best results with a 60% yield in several trials.

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[10] Clemmensen, *Ber.*, **47**, 51 (1914).

[11] Johnson and Hodge, THIS JOURNAL. **35**, 1020 (1913).

The bromine was added slowly through a dropping funnel, and the mixture allowed to stand for several hours The ether was then permitted to evaporate slowly, leaving clumps of characteristic wavy buttons. These were dissolved in alcohol, and crystallized by the procedure outlined above, giving crystals melting at 73.5–74.5°. A mixed melting point, taken using equal parts of the compound prepared by the two methods, did not vary by more than a half degree from the melting points of the two separate 'samples.

Anal. Calcd. for $C_8H_8O_2Br_2$: Br, 54.01. Found: Br, 54.25, 53.88.

The compound is very slightly soluble in water, but readily soluble in most other solvents.

Dichloro-2,4-dihydroxyethylbenzene.—Dichlororesacetophenone (m. p. 190–193") was reduced and purified by the same method used with the dibromo derivative. The crystals are small snow-white prisms, which become opaque on standing. Crystallized from alcohol, the crystals melt at 78–79".

Anal. Calcd. for $C_8H_8O_2Cl_2$: Cl, 34.26. Found: Cl, 33.95, 34.04.

The compound is soluble in the same solvents as the dibromo derivative, but it is somewhat more readily soluble in water than any of the other compounds prepared in this study.

Attempts were made to prepare the conipound by chlorination of ethylresorcinol in acetic acid and other solvents. The same compound apparently was formed, but owing to its solubility in water and other solvents, it proved more difficult to purify than when prepared by the reduction method.

3,5-Dibromo-2,4-dihydroxy-1-propylbenzene.—When propylresorcinol was brominated in acetic acid solution, on dilution an oil separated, which was washed and its alcoholic solution refluxed with animal charcoal, then filtered and the filtrate diluted. No crystals were formed, so the solution was evaporated to dryness on a steam-bath, and the residue cooled with ice. This gave buttons of waxy crystalline material similar to those of the dibromo-ethylresorcinol. Working at zero temperature, a few white crystals were obtained, but these soon melted to a pale brown oil. Attempts were made to obtain a crystallizable product by reduction of the dibromopropionylresorcinol, using the Clemmensen method. This also gave a pale brown oil, which was dissolved in alcohol and water, and cooled to 0° for several hours, when fine white needles formed. The needles melted at the same temperature as those obtained by the bromination method. Owing to the limited quantity and difficulty of separating from the solvent, the compound was not analyzed.

Tribromo-2,4-dihydroxy-1-propylbenzene.—Tribromopropionylresorcinol (m. p. 157") was reduced by the Clemmensen method. The reduction was complete, as indicated by the ferric chloride test. On extraction with ether and distilling off the solvent the residue was dissolved in alcohol and refluxed with animal charcoal. On dilution a yellow oil was obtained which did not crystallize when kept at zero temperature for several days. The compound is being investigated further.

Reduction of Tetrabromoresacetophenone.—Ten grams of tetrabromoresacetophenone was refluxed in 300 cc. of hydrochloric acid (20%) with the Clemmensen reagent. At the end of thirty minutes the solution gave a yellowish-green color when tested with ferric chloride solution, indicating complete reduction of the carbonyl group. The solution was saturated with salt, cooled and extracted with ether. On evaporation of the ether an oil remained which was recrystallized from alcohol and water, giving long silky crystals melting at 74–75'. As the appearance and melting point corresponded closely to those of dibromo-ethylresorcinol,a mixed melting point was made and gave 74–75°, indicating that the two compounds were identical. Two of the bromine atoms of tetrabromoresacetophenoue must therefore be in the methyl group of the side chain of the ketone, since the 3,5-dibromo-2,4-dihydroxy-1-ethylbenzene was prepared by reduction of 3,5-dibromo-2,4-dihydroxyacetophenone.

Summary

1. Improvements in methods of preparation and purification of acyl and alkyl resorcinols are reported.
2. Six new halogen derivatives of acyl and alkyl resorcinols were prepared and their properties described.
3. Evidence was presented to establish the position of the bromine atoms in dibromo-ethylresorcinol and tetrabromoresacetophenone.

PULLMAN, WASHINGTON

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

NAPHTHOL STUDIES. I. THE BROMINATION OF 1,5-DIHYDROXYNAPHTHALENE

BY ALVIN S. WHEELER AND DAVID R. ERGLE[1]

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The halogenation of juglone was first investigated by Wheeler and Scott.[2] Two atoms of chlorine entered the quinone nucleus when chlorination took place in warm glacial acetic acid. However, under like conditions three atoms of bromine were substituted in the molecule. Only a dichloro and a tribromo derivative could be obtained by direct action of the halogens. Attention has now been turned to the halogenation of the dihydric naphthol, 1,5-dihydroxynaphthalene, from which by oxidation with chromic acid, juglone is obtained. By varying the conditions we have introduced into the nuclei two, three and four atoms of bromine, whereas in another study now in progress in this Laboratory only two and three atoms of chlorine have been introduced into the rings. These halogenated naphthols have been oxidized to halogenated naphthoquinones, but none of them corresponds to the halogenated juglones.

The commercial raw material, the dihydroxynaphthalene, was purified by recrystallization from hot water. For bromination glacial acetic acid solutions were used for preparing the dibromo and tribromo derivatives. Iodine was used as a catalyst and a temperature of 80° was necessary in order to obtain the best yields. In order to introduce four atoms of bromine, a chloroform solution of the diacetate was necessary, a catalyst such as iodine and six moles of bromine.

We believe that the structures indicated in the charts are the correct ones

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[1] This paper is a portion of a thesis presented by David R. Ergle to the Faculty of the University of North Carolina in partial fulfilment of the requirements for the degree of Doctor of Philosophy in 1930.

[2] Wheeler and Scott, THIS JOURNAL, 41, 833 (1919).

for these new compounds. The bromine atoms in the dibromo compound B are placed in the beta positions since we are dealing with naphthols. The naphthoquinone C is undoubtedly a para quinone since this isomer forms so readily in general. The tribromo naphthoquinone has been proved to be such (see below). In the dibromo compound it is clear that one bromine atom is in the quinone ring since one is readily replaced by the aniline radical. As for the tribromo compound K, the third bromine atom enters para to the hydroxyl group. In this compound positions 4 and 8 are identical. The bromine atoms in the tetrabromo compound S are placed in positiohs 2,4,6,8, making this a symmetrical molecule. Its oxidation by chromic acid yields a naphthoquinone which is a para quinone, the bromine atom in position 4 being lost in the process. For final proof of its structure the naphthoquinone was found to yield a pyroboracetate ester, a reaction which ties an hydroxyl group to *a* carbonyl group only when these are ortho to each other, as shown by Dimroth and Faust[3] and later by Dimroth.[4]

When five moles of bromine were used and the reaction mixture was kept at room temperature, the dibromo compound was first formed and much later the tetrabromo derivative. However, one of the two acetyl groups in R was hydrolyzed, as proved by the formation of a monobenzoate, V.

The dibromohydroxynaphthoquinone C is not identical with but is isomeric with the 2,3-dibromojuglone (m. p. 167°) of Wheeler and Naiman.[5] The tribromohydroxynaphthoquinone L likewise is an isomer of the tribromojuglone (m. p. 170°) of Wheeler and Scott.[6]

Experimental

Dibromodihydroxynaphthalene

Purification of **1,5-Dihydroxynaphthalene.**—Thirty grams of the commercial product was made into a thick paste with water, suspended in 3 liters of water containing 200 cc. of methyl alcohol and boiled under a reflux for three hours. After cooling to 80° it was saturated with sulfur dioxide and then digested below the boiling point for an hour. It was filtered on a large fast filtering paper in a hot water funnel, the filtrate falling on crushed ice; nearly colorless needles, m. p. 258°; yield, 15–20 g.

2,6-Dibromo-1,5-dihydroxynaphthalene, $C_{10}H_4(OH)_2Br_2$(B).—This compound was first made at room temperature but the yield was greatly increased when the temperature was elevated; 10 g. of dihydroxynaphthalene was dissolved in 350 cc. of glacial acetic acid, a few small crystals of iodine were added and, while the solution was stirred and kept at 80°, 6.5 cc. of bromine (2 moles) dissolved in 25 cc. of glacial acetic acid was added dropwise during the course of thirty minutes. On cooling the solution, the product crystallized out in pale olive green needles. It was washed on the filter with petroleum ether; weight, 14.5 g. or 76% of the theoretical yield; colorless needles on

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[3] Dimroth and Faust, Ber., 54, 3021 (1921).

[4] Dimroth, Ann., 446, 108 (1926).

[5] Wheeler and Naiman, This Journal, 44, 2333 (1922).

[6] Wheeler and Scott, *ibid.*, 41, 838 (1919).

recrystallizing from glacial acetic acid. The substance darkens at 200° and does not melt at **300°**. It is soluble in ether and dilute sodium hydroxide, difficultly soluble in chloroform and insoluble in carbon tetrachloride.

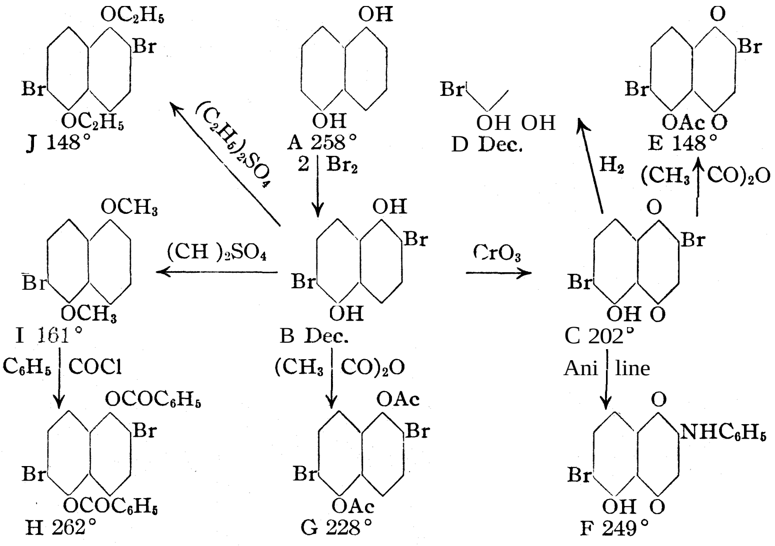
Anal. Calcd. for $C_{10}H_6O_2Br_2$: Br, **50.31.** Found: Br, **50.52**

Diacetate, $C_{10}H_4(OCOCH_3)_2Br_2$(G).—Compound B was heated with an excess of acetic anhydride for an hour at 100°, giving straw yellow needles, colorless on recrystallizing from alcohol; product m. p. **228"**; soluble in ether, benzene and acetic acid; insoluble in petroleum ether.

Anal. Calcd. for $C_{14}H_{10}O_4Br_2$: **Br, 39.80.** Found: Br, **39.68.**

Dimethyl Ester, $C_{10}H_4(OCH_3)_2Br_2$(I).—Compound B was dissolved in 2 moles of dilute sodium hydroxide. To this solution at 60° an excess of **dimethyl** sulfate was added in small amounts until an acid reaction was obtained. More alkali was added and more sulfate but not enough to give an acid reaction. Reddish-purple crystals formed. These were washed on the filter with water. An alcoholic solution with charcoal was boiled until colorless. The filtered solution was concentrated and gave a small amout of colorless microscopic plates which melted at 161°. The **dimethyl** ether is soluble in ether, benzene and chloroform; slightly soluble in cold alcohol and in petroleum ether.

Anal. Calcd. for $C_{12}H_{10}O_2Br_2$: Br, **46.24.** Found: Br. **45.90.**



Diethyl Ether, $C_{10}H_4(OC_2H_5)_2Br_2$(J).—The crude product was a dull red solid. This was dissolved in benzene and boiled. After filtration the solvent was distilled off and the pink residue was recrystallized from hot alcohol as nearly colorless needles, m. p. 148°; soluble in benzene, slightly soluble in cold acetic acid and insoluble in petroleum ether.

Anal. Calcd. for $C_{14}H_{14}O_2Br_2$: Br, **42.89.** Found: Br, **42.77.**

Dibenzoate, $C_{10}H_4(OCOC_6H_5)_2Br_2$(H).—The dibenzoate was prepared by treating a pyridine solution of B with an excess of benzoyl chloride. Much heat was evolved and the whole quickly became a solid mass of yellow crystals. Addition of water gave a heavy yellow oil which was washed with sodium hydroxide and finally with **water.** **Ad-**

dition of alcohol changed the oil to a solid. This was recrystallized from warm pyridine as colorless needles, m. p. 262°; slightly soluble in hot acetic acid; insoluble in ether and in alcohol.

And. Calcd. for $C_{24}H_{14}O_4Br_2$: Br, 30.41. Found: Br, 29.94.

2,6-Dibromo-5-hydroxy-1,4-naphthoquinone, $C_{10}H_3O_2OHBr_2$(C).—To a suspension of 10 g. of B in 200 cc. of glacial acetic acid was added at one time 20 g. of chromic acid dissolved in the smallest amount of water. The mixture turned red, effervesced and the temperature rose to 85°. During the vigorous effervescence, which continued for about fifteen minutes, the material went into solution with a brownish-yellow color. Sometimes it was necessary to start the evolution of gas by warming the mixture. The oxidation was complete when a drop of the solution showed red needles under the microscope, about fifteen minutes in time. After cooling the solution the crystals were filtered off and washed with water; weight, 2.8 g. On recrystallizing from hot acetic acid, the product was obtained in rich red needles, sharply pointed and in clusters; m. p. 202°; soluble in benzene and in chloroform; difficultly soluble in ether and alcohol. It dissolves in alcoholic sodium hydroxide with a purple color which quickly changes to red.

Anal. Calcd. for $C_{10}H_4O_3Br_2$: Br, 48.19. Found: Br, 48.11.

Acetate, $C_{10}H_3O_2(OCOCH_3)Br_2$(E).—The quinone was boiled in acetic anhydride for fifteen hours and the product recrystallized from hot alcohol as golden-yellow needles. m. p. 148°; soluble in acetic acid and insoluble in petroleum ether.

Anal. Calcd. for $C_{12}H_6O_4Br_2$: Br, 42.78. Found: Br, 42.95.

2,6-Dibromo-1,4,5-trihydroxynaphthalene, $C_{10}H_3(OH)_3Br_2$(D).—One gram of C was dissolved in 35 cc. of warm acetic acid. The solution was shaken with additions of zinc dust until the red solution became pale yellow. The filtered solution was dropped upon crushed ice. The crystals so obtained were recrystallized from alcohol by adding water until separation began; colorless needles, darkening at 110° and decomposing at 157°; very soluble in acetic acid, less soluble in carbon tetrachloride and insoluble in petroleum ether; dissolves in dilute sodium hydroxide with a violet coloration, quickly turning to a reddish-brown; readily oxidized back to the quinone with ferric chloride.

Anal. Calcd. for $C_{10}H_6O_3Br_2$: Br, 47.90. Found: Br, 47.74.

6-Bromo-5-hydroxy-2-anilino-1,4-naphthoquinone, $C_{10}H_3O_2OHBrNHC_6H_5$(F).—One-half gram of C was dissolved in 70 cc. of hot alcohol, 1.5 g. of aniline was added and the solution boiled for five minutes. Needles of gun metal luster and red by transmitted light resulted. When heated a red vapor was evolved at 190°. After recrystallization from hot benzene the melting point was 249°.

Anal. Calcd. for $C_{16}H_{10}O_3NBr$: Br. 23.25. Found: Br, 23.27.

Further Notes on Compound **C.**—An attempt was made to prepare the pyroboroacetate ester. A reddish-purple color was obtained and a product which was too unstable to be isolated.

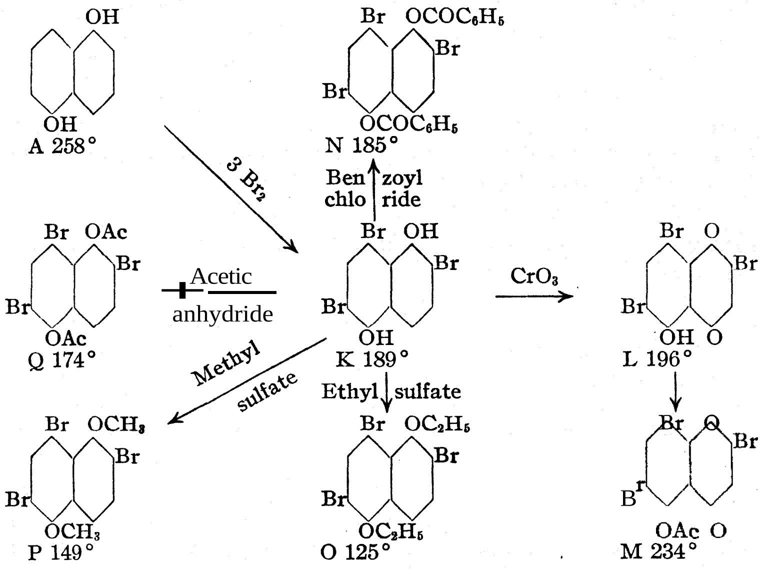
If a glacial acetic acid solution of C is treated with a little concd. nitric acid, short yellow needles crystallize out. This product explodes at 243". It dissolves in dilute sodium hydroxide, giving a red solution which stains the skin. It contains nitrogen but no bromine.

Tribromodihydroxynaphthalene

2,6,8-Tribromo-1,5-dihydroxynaphthalene, $C_{10}H_3(OH)_2Br_3$(K).—Twenty grams of dihydroxynaphthalene was dissolved in 700 cc. of hot glacial acetic acid and a few crystals of iodine added. While the temperature was maintained at 80° a solution of 19.5 cc. of bromine dissolved in 50 cc. of glacial acetic acid was added as follows: 46 cc. was allowed to drop in slowly. Much hydrogen bromide was evolved. One-half of the remainder was added in one portion and after ten minutes the last portion was added slowly. The solution was removed from the water-bath, allowed to stand for fifteen minutes and then cooled. The pale greenish-yellow crystals which formed were **filtered** and washed with petroleum ether; weight, **35** g. or **70.5%** of the theoretical. Purification was effected by dissolving the product in glacial acetic acid at **100°** (decomposes at higher temperatures), shaking with charcoal and filtering. An abundant mass of colorless cotton-like crystals appeared on cooling. The substance melts with decomposition at 189°, is soluble in acetone and in ether, slightly in cold acetic acid and insoluble in petroleum ether.

Anal. Calcd. for $C_{10}H_5O_2Br_3$: Br, 60.45. Found: Br, **60.08.**

It is converted by **concd.** nitric acid into a compound containing nitrogen but no bromine. It consists of yellow needles which explode at **249**" and dissolve in dilute sodium hydroxide with a blood red color.



Diacetate, $C_{10}H_3(OCOCH_3)_2Br_3$(Q).—**Compound** K was boiled for four hours with acetic anhydride, giving yellow needles which became colorless on boiling an alcoholic solution with charcoal; m. p. **174°**; soluble in benzene; insoluble in ether.

Anal. Calcd. for $C_{14}H_9O_4Br_3$: Br, **49.89.** Found: Br, **49.78.**

Dibenzoate, $C_{10}H_3(OCOC_6H_5)_2Br_3$(N).—*Compound* K was treated in pyridine solution with benzoyl chloride. The yellow crystals which formed were changed to an oil with water. The ether solution of the oil was decolorized with charcoal. On mixing the filtered solution with petroleum ether, colorless microscopic plates slowly formed. The substance liquefies with turbidity at 185° but becomes transparent at 189°. **It** is soluble in ether and in chloroform, insoluble in acetic acid, acetone and carbon tetrachloride.

Anal. Calcd. for $C_{24}H_{13}O_4Br_3$: Br, **39.67.** Found: Br, **39.47.**

Dimethyl Ether, $C_{10}H_3(OCH_3)_2Br_3$(P).—The crude product was a reddish-purple solid but in alcoholic solution charcoal removed the color; colorless needles, m. p. **149°**; easily soluble in benzene and in ether. insoluble in petroleum ether.

Anal. Calcd. for $C_{12}H_9O_2Br_3$: Br, 56.47. Found: Br, 56.26.

Diethyl Ether, $C_{10}H_3(OC_2H_5)_2Br_3$(O).—The crude product crystallized from hot alcohol in colorless needles, m. p. 125"; solubilities as above.

Anal. Calcd. for $C_{14}H_{13}O_2Br_3$: Br, 52.98. Found: Br, 52.68.

2,6,8-Tribromo-5-hydroxy-1,4-naphthoquinone, $C_{10}H_3O_2OHBr_3$(L).—To a suspension of compound K dissolved in 250 cc. of glacial acetic acid was added 20 g. of chromic acid dissolved in very little water. The temperature rose to 55°. It was heated to 80° for about fifteen minutes while vigorous effervescence occurred. It was then heated for ten minutes longer. The solution was filtered and poured into much cold water. The orange-colored precipitate was filtered and washed with water. It was dried and extracted with boiling petroleum ether. The solvent was distilled off and the residue recrystallized from hot glacial acetic acid; rich red needles; m. p. 196°; yield, small. The quinone is very soluble in chloroform and in benzene; slightly soluble in alcohol and in ether.

Anal. Calcd. for $C_{10}H_4O_3Br_3$: Br, 58.49. Found: Br, 68.60.

Monoacetate, $C_{10}H_2O_2OCOCH_3Br_3$(M).—The quinone on boiling for seven hours with acetic anhydride gave an acetate consisting of golden-brown scales, m. p. 234". when recrystallized from acetic acid; soluble in chloroform, insoluble in alcohol and in petroleum ether.

Anal. Calcd. for $C_{12}H_5O_4Br_3$: Br, 52.98. Found: Br. 52.84.

Tetrabromodihydroxynaphthalene

2,4,6,8-Tetrabromo-1,5-dihydroxynaphthalene, $C_{10}H_2(OH)_2Br_4$(S).—To 10 g. of diacetoxynaphthalene dissolved in 200 cc. of chloroform containing a few crystals of iodine was added 14 cc. of bromine. The solution was well shaken and allowed to stand. Much hydrogen bromide was evolved. After ten minutes the product began to crystallize out; most of the product had formed in ten hours. This was filtered off and a second crop was obtained at the end of two days; total yield, 19.5 g.; colorless glistening feathery needles which did not melt below 300°. It can be recrystallized from hot benzene, 90 cc. of which dissolves 0.5 g. only. The product decomposes if solvents of higher boiling point are used. It is insoluble in most of the organic solvents. Crystals exposed to direct sunlight turn rose-pink in color within two hours.

Anal. Calcd. for $C_{10}H_4O_2Br_4$: Br, 67.23. Found: Br, 67.45.

Dimethyl Ether, $C_{10}H_2(OCH_3)_2Br_4$(T).—The methyl ether was prepared in the usual way and the crude product boiled in benzene with charcoal. It was then filtered and the solvent evaporated off. The residue was dissolved in the least amount of hot benzene, cooled and an equal amount of alcohol added, giving colorless microscopic needles, m. p. 226°; soluble in benzene and in acetic acid, insoluble in ether and in petroleum ether.

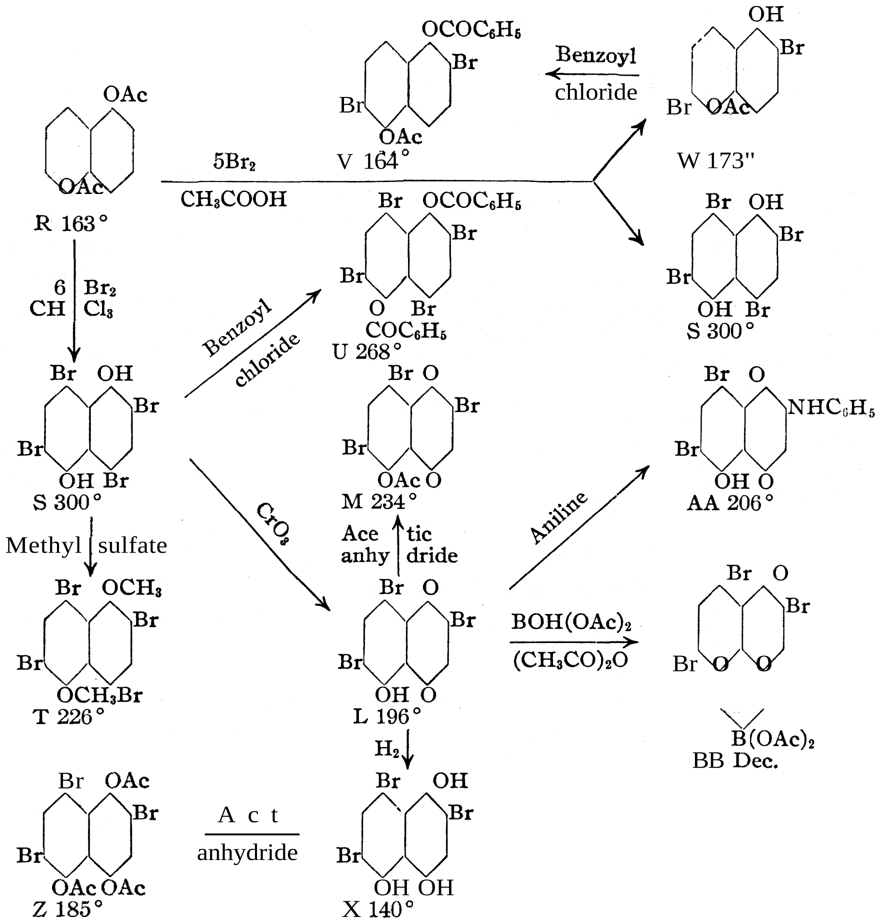
Anal. Calcd. for $C_{12}H_8O_2Br_4$: Br, 63.41. Found: Br, 63.21.

Dibenzoate, $C_{10}H_2(OCOC_6H_5)_2Br_4$(U).—Compound S was benzoylated by the Schotten–Baumann method. The product was purified as was the dimethyl ether. and gave irregularly shaped plates, m. p. 268°; soluble in benzene; insoluble in alcohol and in ether.

Anal. Calcd. for $C_{24}H_{12}O_4Br_4$: Br, 46.92. Found: Br, 46.85.

Further Notes on the Tetrabromonaphthalene.—Compound S was oxidized with chromic acid in acetic acid solution. One atom of bromine was eliminated and a quinone identical with L was obtained, as was shown by its melting point. 196°, by the identity of the acetyl derivatives and by the following analysis.

Anal. Calcd. for $C_{10}H_3O_3Br_3$: Br, 58.39. Found: Br. 58.41.



Compound S gave a product with concd. nitric acid in acetic acid: chrome-yellow needles, m. p. 232" with decomposition. It contains nitrogen but no bromine. It dissolves in dilute sodium hydroxide, the solution coloring the skin red.

Certain dibromo and tribromo derivatives follow since a part of the bromine is eliminated in some reactions.

6,8-Dibromo-2-anilino-5-hydroxy-1,4-naphthoquinone, $C_{10}H_2O_2OHNHC_6H_5Br_2$ (AA).—Two cc. of aniline in 5 cc. of glacial acetic acid was added to a hot solution of 1 g. of L in 40 cc. of acetic acid, giving an abundant yield of dark red glistening needles of hair-like structure, showing a green fluorescence when recrystallized from acetic acid. It melts at 206" is soluble in chloroform and slightly soluble in alcohol and in ether.

Anal. Calcd. for $C_{16}H_9O_3NBr_2$: Br, 37.82. Found: Br, 37.66.

2,6,8-Tribromo-1,4,5-trihydroxynaphthalene, $C_{10}H_2(OH)_3Br_3$ (X).—A suspension of 1 g. of the naphthoquinone L in 50 cc. of ether was underlaid with 50 cc. of dilute sulfuric acid. This was shaken with additions of zinc dust until reduction was complete. The ether layer was separated and mixed with an equal volume of petroleum ether. The crystalline precipitate was purified from a like mixture of solvents as long silky flesh-colored needles which decompose at about 140°, soluble in alcohol and in acetic acid;

difficultly soluble in chloroform and in benzene; soluble in dilute sodium hydroxide with a purple color which changes to a reddish-brown. Ferric chloride oxidizes the naphthol back to the quinone.

Anal. Calcd. for $C_{10}H_5O_3Br_3$: Br, 58.11. Found: Br, 57.75.

Triacetate, $C_{10}H_2(OCOCH_3)_3Br_3$(Z).—Compound X was boiled with acetic anhydride for seven hours: white fluffy needles from alcohol, m. p. 185°; soluble in benzene, less soluble in ether.

Anal. Calcd. for $C_{16}H_{11}O_6Br_3$: Br, 44.53. Found: Br, 44.31.

Pyroboro-acetate Ester of Tribromohydroxy-naphthoquinone (BB).—To 1 g. of compound L dissolved in 50 cc. of warm acetic anhydride was added 0.5 g. of pyroboro-acetate dissolved in the smallest amount of acetic anhydride. The flask was stoppered and shaken. A reddish-purple color developed and a fluorescent solid crystallized on cooling. The product was filtered, washed with absolute ether and dried to constant weight over phosphorus pentoxide; weight, 1.2 g.; hexagonal plates, possessing a green metallic luster but red by transmitted light. The ester was easily and completely decomposed to the original quinone by water. It was affected by even a very short exposure to the atmosphere. When heated a red vapor was evolved at 200° but no melting occurred below 300°.

Anal. Calcd. for $C_{14}H_8O_7Br_3$: Br, 44.54. Found: Br, 44.47.

Determinations were also made for boric acid, acetic acid and for the quinone residue, using the method proposed by Dimroth.[7]

Anal. Calcd. for the quinone residue: 0.4592. Found: 0.4576. Calcd. for acetic acid: 14.9 cc. of 0.1457 N $Ba(OH)_2$. Found: 14.8 cc. Calcd. for boric acid: 7.4 cc. of 0.1457 N $Ba(OH)_2$. Found: 7.4 cc.

Bromination of Diacetoxynaphthalene in Acetic Acid.—When diacetoxynaphthalene is dissolved in glacial acetic acid, treated with 5 moles of bromine and allowed to stand at room temperature, a mixture of products S and W is obtained. The first crop, obtained after a few hours, was found to consist of the naphthol W. The second crop, after twelve hours' standing, was a mixture of W and the tetrabromo compound S. The naphthol was dissolved out from the mixture with acetone. After a week a final crop consisting of S only was recovered. Ten grams of the acetate gave 5 g. of W and 13 *g*. of S.

2,6-Dibromo-5-acetoxy-1-naphthol, $C_{10}H_4OCOCH_3OHBr_2$(W).—Colorless needles, m. p. 173°, from acetic acid solution.

Anal. Calcd. for $C_{12}H_8O_3Br_2$: Br, 44.44. Found: Br, 44.14.

The fact that one acetyl group was hydrolyzed was shown by the preparation of a monobenzoate in pyridine solution.

2,6-Dibromo-5-acetoxy-1-benzoxynaphthalene, $C_{10}H_3(OCOCH_3)(OCOC_6H_5)Br_2$ (V).—This product, made in the usual way, was recrystallized from a mixture of equal parts of alcohol and petroleum ether as transparent colorless rectangular plates, m. p. 164°; soluble in alcohol, slightly soluble in cold acetic acid and in petroleum ether.

Anal. Calcd. for $C_{19}H_{11}O_4Br_2$: Br. 35.57. Found: Br. 35.48.

Summary

1. 1,5-Dihydroxynaphthalene in acetic acid yields with bromine in the presence of iodine a dibromo and a tribromo substitution product.

2. The diacetate in chloroform solution similarly treated gives a tetrabromo derivative.

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[7] Dimroth, *Ann.*, 446, 108 (1926).

3. The diacetate in acetic acid solution at room temperature gives a mixture of the tetrabromo derivative and a dibromo-acetoxynaphthol.
4. The dibromo compound is oxidized by chromic acid to a naphthoquinone; so also is the tribromo derivative, but the tetrabromo compound oxidizes with the loss of one bromine atom to the same quinone.
5. The naphthoquinones are easily reduced to dihydric and trihydric naphthols.
6. The hydroxynaphthoquinones have the 1,4-quinoid structure, as proved by the pyroboro-acetate reagent.
7. A variety of derivatives is described.
8. The naphthoquinones are isomeric with certain halogenated juglones but are not identical with any.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, NATIONAL TSINGHUA UNIVERSITY]

LEVULINIC ACID AND ITS ESTERS

BY PETER P. T. SAH AND SHAO-YUAN MA

RECEIVED JUNE 27, 1930 PUBLISHED DECEMBER 18, 1930

While levulinic acid[1] is formed quite easily from glucose and other carbohydrates by the action of boiling dilute mineral acids, the mechanism of the reaction is still obscure and there is practically no good convenient method for the preparation of a large amount of the acid in the laboratory. The common procedure described by Rischbieth[2] offers experimental difficulties and gives only low yields due to incomplete disintegration of the carbohydrate (starch). McKenzie[3] has recently described a procedure in which cane sugar is hydrolyzed with dilute hydrochloric acid, the solution is evaporated to dryness and the residue extracted with ether. We have not found that the new method has any advantage over those previously described.

By repeated trials we have found commercial glucose to be a better starting material than sucrose. The yields were higher and the amount of humus substance precipitated was comparatively less. Another experimental observation we have made is that the action proceeds rapidly if the temperature of the solution is raised to 110°. At temperatures below this,

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[1] (a) Nöldecke, Ann., 149, 224 (1869); (b) v. Grote and Tollens, *ibid.*, 175, 181 (1875); (c) v. Grote, Kehrer and Tollens, *ibid.*, 206, 207, 226, 233, 257 (1881); (d) Tollens, *Ber.*, 14, 1950 (1881); (e) Kent and Tollens, Ann., 227, 227 (1884); (f) Block, Kreckeler and Tollens, *ibid.*, 238, 287 (1887); (g) Wehmer and Tollens, *ibid.*, 243, 314 (1888); (h) Schuette and Sah, THIS JOURNAL, 48, 3164 (1926).

[2] Rischbieth, *Ber.*, 20, 1773 (1887).

[3] McKenzie, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1929, Vol. IX, p. 50.

the transformation of hexose to levulinic acid is very slow and incomplete and a large amount of intermediate decomposition product, oxymethylfurfural, accumulates and is lost owing to volatilization on subsequent distillation or evaporation.

Although there are quite a few functional derivatives of levulinic acid described in the literature, the number is still rather small. Of the esters,* only three, methyl, ethyl and n-propyl, have been synthesized. The ethyl ester has been quite thoroughly studied; the other two are only briefly described. We have synthesized seven esters of levulinic acid, namely, methyl, ethyl; n-propyl, isopropyl, n-butyl, isobutyl and isoamyl levulinates, thus adding four new esters to the list already described. These esters were highly purified and a few of their important physical constants determined. To characterize them, we have also prepared the corresponding semicarbazones and phenylhydrazones. Their melting points and nitrogen contents were accurately determined.

Experimental

Preparation of **Levulinic** Acid.—Five hundred cc. of commercial concentrated hydrochloric acid was mixed in a 2-liter beaker with an equal volume of water. The acid solution was heated to boiling and 500 g. of commercial glucose (solid, technical lumps from E. Merck, Darmstadt) was added in small portions with constant stirring. The solution was boiled gently for ten minutes. After cooling, the large amount of humus material was filtered off by suction. The filtrate was transferred to a 3-liter round-bottomed flask and refluxed vigorously for at least twenty-four hours, in order to convert the intermediate product, oxymethylfurfural, to levulinic acid. The humus material further precipitated out was filtered off from time to time. The filtrate was distilled at atmospheric pressure until the thermometer registered at 125". The hydrochloric acid solution thus recovered could be used over again. The residue, after filtration, was distilled under reduced pressure. The fraction boiling from 146 to 184° at 7 mm. pressure was collected and redistilled. Upon chilling, the practically colorless liquid solidified to large, glassy, shining crystals, m. p. 33–35°; b. p. 245–246°; b. p. 145° at 4 mm.; yield, about 150 g. from 1 kilo of glucose used. The acid was freely soluble in water, ethyl alcohol or ether.

Esterification.—The acid was esterified directly with excess of absolute alcohol (methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, or isoamyl) in the presence of a small amount of hydrochloric acid. The procedure described by Adkins and McElvain[5] for the preparation of ethyl benzoate was adopted. The yield was about 65% of the theoretical. The tables show the simple physical constants and the chemical analysis of the various esters prepared. These liquids, colorless and with faint pleasant odor, are insoluble in water (except methyl levulinate), soluble in alcohol, benzene or carbon bisulfide, and very soluble in ether, chloroform, carbon tetrachloride or ethyl acetate.

Preparation of **Semicarbazones.**—The procedure recommended by Baeyer[6] was followed. To a solution of semicarbazide hydrochloride of known strength, the calculated amount of potassium acetate in alcohol and the ester of levulinic acid were added.

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[4] (a) V. Grote, Kehrer and Tollens, Ann., 206, 220–222 (1881); (b) Conrad, *ibid.*, 188,225 (1877); (c) Michael, J. *prakt. Chem.*, [2] 44, 114 (1891).

[5] Adkins and McElvain, "Practice of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1st ed., 1925, p. 221.

[6] Baeyer, Ber., 27, 1918 (1894).

TABLE I

SIMPLE CONSTANTS OF ALKYL LEVULINATES

Levulinates	B. p., °C.	d_4^{20}	n_D^{20}	Molecular refraction Gladstone and Dale Obs.	Calcd.	Lorentz and Lorenz Obs.	Calcd.
Methyl	191–193	1.05113	1.4231	52.36	52.27	31.52	31.77
Ethyl	199–201	1.01336	1.4225	60.08	59.92	36.17	36.37
Isopropyl	203–205	0.98422	1.4220	67.79	67.57	40.83	40.97
n-Propyl	214–216	.98988	1.4255	67.96	67.57	40.88	40.97
Isobutyl	222–224	.97047	1.4264	75.63	75.22	45.48	45.57
n-Butyl	229–231	.97452	1.4290	75.77	75.22	45.53	45.57
Iso-amyl	238–240	.95921	1.4310	83.64	82.87	50.23	50.17

TABLE II

ANALYSIS OF ALKYL LEVULINATES

Alkyl	Formula	Hydrogen, % Calcd.	Found	Carbon, % Calcd.	Found	Saponification no. Calcd.	Found
Methyl	$C_6H_{10}O_3$	7.75	7.70	55.35	54.84	431.3	427.4
Ethyl	$C_7H_{12}O_3$	8.39	7.91	58.30	57.84	389.3	392.9
Isopropyl	$C_8H_{14}O_3$	8.92	8.60	60.72	60.45	354.8	357.9
Propyl	$C_8H_{14}O_3$	8.92	9.23	60.72	60.57	354.8	351.3
Isobutyl	$C_9H_{16}O_3$	9.37	9.00	62.75	62.59	325.9	324.7
Butyl	$C_9H_{16}O_3$	9.37	9.81	62.75	63.22	325.9	322.4
Isoamyl	$C_{10}H_{18}O_3$	9.74	10.14	64.47	64.12	301.4	297.5

The methyl and ethyl esters reacted very quickly. Their semicarbazones precipitated almost instantaneously upon shaking. The higher homologs were allowed to stand overnight, whereby beautiful crystals came out smoothly. They were white solids with definite crystalline structure, insoluble in water, only difficultly soluble in ether, carbon bisulfide or carbon tetrachloride, soluble in ethyl alcohol, ethyl acetate or benzene and very soluble in chloroform.

For analysis and melting point determinations, the pure crystals were filtered off by suction, washed with a small amount of distilled water and dried in a vacuum over sulfuric acid. The nitrogen content was found by the Dumas method.

TABLE III

MELTING POINTS AND ANALYSES OF SEMICARBAZONES

Alkyl	Formula	M. p., °C.	Subs., g.	N_2, cc.	P, mm. (corr)	T, °C.	Nitrogen, % Calcd	Found
Methyl	$C_7H_{13}N_3O_3$	142–143	0.0606	11.9	747.25	17.7	22.46	22.68
Ethyl	$C_8H_{15}N_3O_3$	147–148	.0422	7.4	749.54	11.0	20.89	20.79
Propyl	$C_9H_{17}N_3O_3$	129–130	.0620	10.8	736.3	17.0	19.53	19.87
Isopropyl	$C_9H_{17}N_3O_3$	141–142	.0470	8.1	736.7	21.0	19.53	19.40
Butyl	$C_{10}H_{19}N_3O_3$	102–103	.0512	8.4	737.1	19.0	18.34	18.61
Isobutyl	$C_{10}H_{19}N_3O_3$	112–113	.0520	8.3	740.1	15.0	18.34	18.43
Isoamyl	$C_{11}H_{21}N_3O_3$	91–92	.0610	9.5	737.6	16.0	17.28	17.86

Preparation of Phenylhydrazones.—The procedure described by Michael[4c] was followed. A saturated solution of phenylhydrazine hydrochloride was prepared by dissolving the hydrochloride in about twelve parts of water. A molecular equivalent of alkyl levulinate was then added to the solution. Upon shaking and then standing for a few hours, crystals of the hydrazones separated out. They were filtered off by suction, pressed between filter paper and then dried in a vacuum over sulfuric acid to constant weight. The crystals were colorless when freshly prepared. On exposure to air, they turned yellowish-brown, showing that they were unstable toward oxygen. For melting point determination and analysis, the compound must be freshly prepared and recrystallized from benzene. The hydrazones of alkyl levulinates were insoluble in water, soluble in ether, alcohol or carbon tetrachloride, and very soluble in benzene, carbon bisulfide, chloroform or ethyl acetate. Their nitrogen content was analyzed for by the Dumas method.

TABLE IV

MELTING POINTS AND ANALYSES OF PHENYLHYDRAZONES

Alkyl	Formula	M. p., °C.	Subs, g.	N_2, *cc.*	P, mm. (con-.)	*T*, °C.	Nitrogen, %	
							Calcd.	Found
Methyl	$C_{12}H_{16}N_2O_2$	94–96	0.0322	3.7	738 2	18.0	12 73	13.10
Ethyl	$C_{13}H_{18}N_2O_2$	103–104	,1142	11.8	737.4	15.0	11.97	11.89
Propyl	$C_{14}H_{20}N_2O_2$	88–90	.0920	8.9	748 6	17.0	11.29	11.22
Isopropyl	$C_{14}H_{20}N_2O_2$	108–109	.0882	8.4	740.2	18.5	11.29	10.87
Butyl	$C_{15}H_{22}N_2O_2$	79-81	.1182	11.3	737.5	17.0	10.69	10 92
Isobutyl	$C_{15}H_{22}N_2O_2$	84–86	.1062	10.0	748.5	16.0	10.69	10.96
Isoamyl	$C_{16}H_{24}N_2O_2$	70–72	.0616	5.3	750.3	15.0	10.14	10.07

Acknowledgment.—The authors wish to thank Dr. Albert Carruthers of the Department of Biochemistry, Peking Union Medical College, and Professor Tsun Chang, Head of the Chemistry Department, for their kind and valuable criticisms.

Summary

1. A simple procedure for the preparation of levulinic acid from commercial glucose is described.

2. Seven alkyl levulinates (three previously described and four new compounds) have been synthesized by direct esterification of levulinic acid with various alcohols. The esters were obtained highly pure and their simple constants studied.

3. These esters were characterized by their corresponding semicarbazones and phenylhydrazones. Among these, only the ethyl derivatives were previously described.

NATIONAL TSINGHUA UNIVERSITY
PEIPING-WEST, CHINA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

STUDIES IN THE ANTHRONE SERIES.
I. THE CONDENSATION OF PHTHALIDE WITH AROMATIC COMPOUNDS[1]

BY AL STEYERMARK WITH JOHN H. GARDNER

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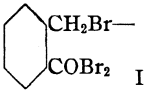
In view of the importance in medicine of certain anthrones and dianthrones such as those found in chrysarobin, it has seemed of interest to study methods for the determination of the structures of members of this class of compounds. Most of the work which has been done heretofore has been purely analytical in nature and consequently cannot be regarded as furnishing a final solution of the problem. The present work represents the beginning of a series of studies on the methods of synthesizing anthrones and the rules of orientation involved.

It was shown by Mayer and Fischbach[2] that w-bromo-o-toluyl bromide (I) can be condensed with benzene by means of aluminum chloride to form anthrone (II). Using chlorobenzene, they obtained a product which they identified as 2-chloro-9-anthrone (III).



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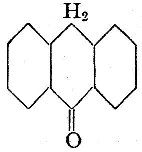

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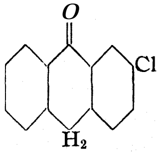
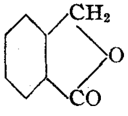


III

Since phthalide (IV) is related to w-bromo-o-toluyl bromide as an acid anhydride to its bromide, it would be expected to undergo the same type of condensation reactions. As a matter of fact, King[3] obtained *o*-benzylbenzoic acid (V) by the condensation of phthalide with benzene. In the present investigation, it has been found that anthrone is formed in this reaction in somewhat greater quantities than the benzylbenzoic acid.



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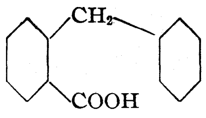

V

In view of the work of Mayer and Fischbach and of King, and by analogy with the product obtained in the condensation of phthalic anhydride with toluene,[4] it would be expected that phthalide could be condensed with

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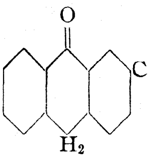
[1] Based upon a portion of a thesis submitted by Al Steyermark, Fellow in Chemistry and Physics, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Washington University, June, 1930.

[2] Mayer and Fischbach, Ber., 58, 1251 (1925).

[3] King, THIS JOURNAL, 49, 662 (1927).

[4] Friedel and Crafts, *Ann. chim. plays.*, [6] 14, 447 (1888).

toluene with the formation of 2-methyl-9-anthrone (VI) and possibly o-(4-methylbenzyl)-benzoic acid (VII) as the principal products. However, on carrying out the reaction, the product was an oily mass, obviously a mixture, since all of the compounds which might have been expected to be formed are solids. On attempting to work up the product, a small amount of unchanged phthalide was the only pure substance which could be isolated. The crude product on oxidation gave a good yield of 2-methylanthraquinone (VIII), indicating the presence of either 2-methyl-9-anthrone (VI) or 2-methyl-10-anthrone (IX) or both.



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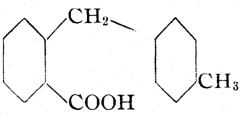

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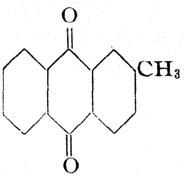
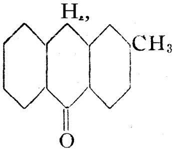
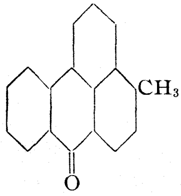


VIII

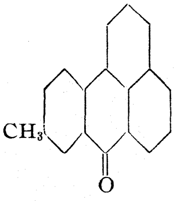


IX

As both isomers melt at practically the same temperature, it would be expected that they would exhibit practically the same solubilities in all solvents and consequently it would be impossible to separate them by fractional crystallization. This we have found to be the case. However, the benzanthrones which can be obtained from them[5] melt 30° apart and would be expected to differ markedly in their solubility relationships. This was found to be the case. 2-Methylbenzanthrone (X), m. p. 199°, is easily crystallized from a mixture of benzene and petroleum ether, while the isomeric 6-methylbenzanthrone (XI), m. p. 170°, is too soluble in benzene to be crystallized readily from it or from a mixture of benzene and petroleum ether.



X



XI

The oily mixture obtained from the condensation of phthalide with toluene was treated with glycerol and sulfuric acid and the product subjected to fractional crystallization from a mixture of benzene and petroleum ether. In this way, 2-methylbenzanthrone (X) was isolated, showing that

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[5] Steyermark with Gardner, This Journal, 52,4887 (1930).

2-methyl-10-anthrone was present in the original condensation product. From the character of that material and by analogy with the work of Mayer and Fischbach and of King, it is certain that the isomeric 2-methyl-9-anthrone was also formed, but it was found impossible to isolate it or the benzanthrone formed from it in the reaction with glycerol and sulfuric acid.

On condensing phthalide with chlorobenzene, there was obtained a red, oily mass which, on oxidation, yielded 2-chloro-anthraquinone, indicating the presence of either 2-chloro-9-anthrone or 2-chloro-10-anthrone or both. In this case neither the anthrones nor the corresponding benzanthrones could be isolated in a sufficiently pure state for identification. All indications point to the presence of both possible isomers.

From the results of Mayer and Fischbach and of King, it would be concluded that the condensation of phthalide with aromatic hydrocarbons and their derivatives takes place exclusively through the methylene group of phthalide with the formation of o-benzylbenzoic acids which may be dehydrated to anthrones. The present work demonstrates that the carboxyl residue also reacts, leading to the formation of benzoylbenzyl alcohols, which are dehydrated to anthrones.

Experimental

Anthrone.—Ten grams of phthalide was dissolved in 50 cc. of benzene in a 500-cc. flask provided with a reflux condenser and protected by a calcium chloride tube; 20 g. of anhydrous aluminum chloride was added and the mixture heated on the water-bath for ten hours. After cooling, 100 cc. of 1:1 hydrochloric acid was added and the excess benzene driven off with steam. The residue was cooled and the solid material filtered off; yield of light yellow needles from alcohol followed by recrystallization from 3:1 benzene–petroleum ether, 4 g. (28%), m. p. 152–154°. A mixed melting point with anthrone showed no depression.

For further identification, a portion was oxidized with chromic acid in glacial acetic acid, yielding anthraquinone, m. p. 282–284°. Another portion was methylated by the method of Meyer and Schlosser[6] to 9-anthranol methyl ether, m. p. 94–95°.

Condensation of Phthalide with Toluene.—A mixture of 15 g. of phthalide in 90 cc. of toluene with 30 g. of anhydrous aluminum chloride was heated for fifteen hours on the steam-bath. On working up the product as was done with anthrone, there was obtained an oily mass from which no pure compound could be isolated.

Oxidation of the Phthalide–Toluene Condensation Product.—Two grams of the crude product was dissolved in 15 cc. of glacial acetic acid and a solution of 0.6 g. of chromic acid in 6 cc. of 50% acetic acid was added. After heating on the water-bath for five minutes, the product was precipitated by the addition of water, giving nearly colorless needles from alcohol, m. p. 168–170°. A mixed melting point with 2-methylanthraquinone showed no depression.

Preparation of 2-Methylbenzanthrone from the Phthalide–Toluene Condensation Product.—The oily mass obtained in the condensation described above was dissolved in 150 cc. of 82% sulfuric acid and 20 g. of glycerol was added. The mixture was heated in an oil-bath at 125–130° for four hours. The red solution was then poured onto

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[6] Meyer and Schlosser, *Ann.*, 420, 126 (1920).

cracked ice. The olive-green precipitate was extracted with 500 cc. of hot 1% sodium hydroxide solution. After washing with water and drying, the residue was extracted with hot benzene. After cooling and adding petroleum ether, the benzene extract deposited 3.5 g. of yellow needles of 2-methylbenzanthrone, m. p. 198.5–199°, from benzene and petroleum ether. A mixed melting point with 2-methylbenzanthrone prepared from 2-methyl-9-anthroxle showed no depression.[5]

Anal. Subs., 0.1033: CO_2, 0.3403; H_2O, 0.0444. Calcd. for $C_{18}H_{12}O$; C, 88.49; H, 4.91. Found: C, 88.35; H, 4.81.

Condensation of Phthalide with **Chlorobenzene.**—A mixture of 10 g. of phthalide in 55 cc. of chlorobenzene with 20 g of anhydrous aluminum chloride was heated in an oil-bath at 125–130° for fifteen hours. The resulting product was worked up as before. No pure compound could be isolated.

A portion of the crude condensation product on oxidation with chromic acid gave 2-chloro-anthraquinone, m. p. 206–207°. On attempting to prepare a chlorobenzanthrone, a mixture which could not be separated into its components was obtained.

Summary

1. Phthalide can be condensed with aromatic hydrocarbons and their derivatives with the formation of anthrones.

2. Condensation takes place both through the methylene and the carboxyl residues of phthalide resulting in the formation of a mixture of isomers and rendering the method unsuitable for the synthesis of anthrones of definite structure.

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

STUDIES IN THE ANTHRONE SERIES.
II. THE SYNTHESIS OF SOME HYDROXYMETHYLANTHRONES[1]

BY AL STEYERMARK WITH JOHN H. GARDNER

RECEIVED JUNE 30, 1930 PUBLISHED DECEMBER 18, 1930

Since the most important of the naturally occurring anthrones are derived from 1,8-dihydroxy-3-methylanthraquinone and some related compounds, it has seemed of interest to study methods for the synthesis of hydroxy- and hydroxymethylanthrones which will afford definite proof of the structures of the products obtained. Most of the work which has been done on the determination of the structure of this class of compounds has been analytical in nature and has not always led to concordant results.[2] The only synthetic method which has been extensively investigated is the phthalaldehyde acid condensation method originated by Bistrzycki, which has been extended and improved by Adams and his students. The

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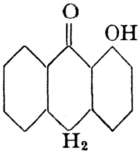
[1] Based upon a portion of a thesis submitted by Al Steyermark, Fellow in Chemistry and Physics, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Washington University, June, 1930.

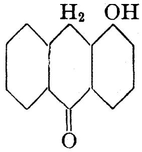
[2] Cross and Perkin, J. *Chem. Soc.*, 292 (1930), and previous papers by Perkin and his co-workers; Green. ibid.. 2341 (1927).

number of compounds obtainable in this way is distinctly limited owing to the[3] difficulty of preparing suitable substituted phthalaldehyde acids.

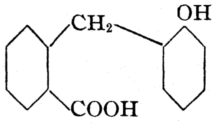
The most commonly used method for the preparation of anthrones has been the reduction of the corresponding anthraquinone with tin and hydrochloric acid in glacial acetic acid solution. This method was applied to 1-hydroxyanthraquinone by Liebermann and Mamlock and by Meyer and Sander,[4] but no satisfactory evidence as to the structure of the product obtained was presented until Cross and Perkin[6] showed that the benzanthrone which was obtained from it could not be methylated with methyl iodide and alkali, indicating that the carbonyl and hydroxyl groups are adjacent to each other. From this it must be concluded that the product is 1-hydroxy-9-anthrone (I). In the same paper they describe the preparation of an isomer, presumably 1-hydroxy-10-anthrone (11), obtained by the reduction of the acetate of 1-hydroxyanthraquinone.[6]



I



II



III

In this work the first step was the confirmation of the conclusions of Cross and Perkin by direct synthesis. o-(2-Hydroxybenzoyl)-benzoic acid was reduced to o-(2-hydroxybenzyl)-benzoic acid (III), which was in turn dehydrated to 1-hydroxy-10-anthrone. This compound, which formed colorless needles melting at 241–2°, agreed in all of its properties with the compound obtained by Cross and Perkin by the reduction of the acetate of 1-hydroxyanthraquinone. The compound obtained on the reduction of 1-hydroxyanthraquinone itself, however, formed canary yellow needles melting at 137.5–138° and consequently can be only 1-hydroxy-9-anthrone. From this it is concluded that the hydroxyl group in the a-position of the anthraquinone molecule directs the reduction to the carbonyl group farthest removed.

By a similar method, Barnett and Goodway[7] showed that the reduction of 2-methylanthraquinone yields a mixture of both possible isomeric methylanthrones. A repetition and extension of their work indicates that by far the major part of the product is 2-methyl-10-anthrone (IV) since only 2-methylbenzanthrone (V) can be obtained from the crude mix-

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[3] Brubaker and Adams, This Journal, 49, 2279 (1927), give a bibliography of the work in this field.

[4] Liebermann and Marnlock, *Ber.*, 38, 1784 (1905); Meyer and Sander, Ann., 420, 113 (1920).

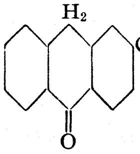
[5] Cross and Perkin, J. Chem. *Soc.*, 292 (1930).

[6] Ref. 5, p. 306.

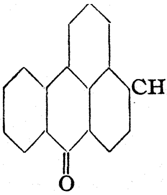
[7] Barnett and Goodway, ibid., 1754 (1929).

ture. Using pure 2-methyl-10-anthrone there was no increase in the yield of 2-methylbenzanthrone.[4] Consequently, we may conclude that the methyl group in the β-position in the anthraquinone molecule directs the reduction to the carbonyl group in the meta position of its ring.

Since the reduction of 1-hydroxyanthraquinone yields a single product and that of 2-methylanthraquinone a mixture, it would be expected that when the orienting influences of the two groups conflict, the hydroxyl group would dominate. This could be tested in the reduction of 1-hydroxy-2-methylanthraquinone.

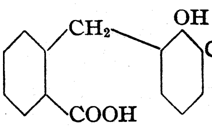


IV

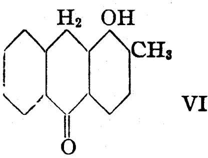


V

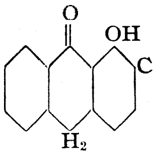
By the reduction of o-(2-hydroxy-3-methylbenzoyl)-benzoic acid, there was obtained o-(2-hydroxy-3-methylbenzyl)-benzoic acid (VI). This compound, by treatment with sulfuric acid, yielded 1-hydroxy-2-methyl-10-anthrone (VII) as colorless needles melting at 207.2–208°. On reducing 1-hydroxy-2-methylanthraquinone there was obtained an anthrone which crystallized in the form of yellow needles melting at 136.2–137° and which must be 1-hydroxy-2-methyl-9-anthrone (VIII), showing that the hydroxyl group has a stronger directive influence in the reduction of the carbonyl group of an anthraquinone derivative than does the methyl group, as was expected.



VI



VII

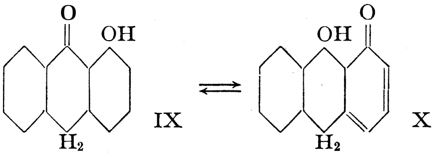


VIII

In the same way, the reduction of 1-hydroxy-3- and 4-methylanthraquinone was investigated. In each case the corresponding methyl-1-hydroxy-9-anthrone was obtained. Both of these anthrones crystallized as canary yellow needles.

By dehydration of o-(2-hydroxy-4-methylbenzyl)-and o-(2-hydroxy-5-methylbenzyl)-benzoic acid, there were obtained 1-hydroxy-3- and 1-hydroxy-4-methyl-10-anthrone, both forming light colored or colorless needles melting at much higher temperatures than the isomeric 1-hydroxy-9-anthrones.

It is of interest to note that the 1-hydroxy-9-anthrones are in every case colored while the isomeric 1-hydroxy-10-anthrones are, with one exception, colorless. 1-Hydroxy-3-methyl-10-anthrone could never be obtained entirely colorless, but the best samples which were obtained appeared to be slightly impure and it is believed that the color would be removed on complete purification. It seems reasonable to believe that the color of the 1-hydroxy-9-anthrones may be due to a benzenoid–quinoid tautomerism such as has been suggested for the hydroxyanthraquinones and demonstrated in one case,[8] the two forms represented by Formulas IX and X being in equilibrium.



Experimental

2-Methyl-10-anthrone.—2-Methylanthraquinone was reduced to the mixture of anthrones by the method of Barnett and Goodway.[9] After five recrystallizations from alcohol there was obtained an 8.8% yield of 2-methyl-10-anthrone, m. p. 101–102°.

2-Methyl-9-anthrone.—The isomeric 2-methyl-9-anthrone was obtained from p-toluyl-o-benzoic acid by the method of Limpricht.[10] The product melted at 102–103° and showed the same solubilities in alcohol, benzene, petroleum ether and various other solvents as 2-methyl-10-anthrone, explaining the extreme difficulty found in the separation of the two isomers.

2-Methylbenzanthrone.—Three grams of the crude mixture of methylanthrones obtained in the reduction of 2-methylanthraquinone was converted into the benzanthrone by the method of Scholl and Seer.[11] After recrystallization from a mixture of benzene and petroleum ether there was obtained 1 g. of 2-methylbenzanthrone, m. p. 198–199°. None of the isomeric 6-methylbenzanthrone could be isolated. Using pure 2-methyl-10-anthrone did not increase the yield.

o-(2-Hydroxybenzoyl)-benzoic Acid and its Homologs.—Phthalic anhydride was condensed with phenol and with the three cresols according to the procedure of Ullmann and Schmidt.[12] In this way there were obtained o-(2-hydroxybenzoyl)-benzoic acid and the three isomeric o-(2-hydroxymethylbenzoyl)-benzoic acids. It was noted, however, that, contrary to the results of Ullmann and Schmidt, on condensing phthalic anhydride with phenol and with o-cresol, there was formed a larger proportion of the benzoylbenzoic acid in which the condensation had taken place in the position para to the hydroxyl group than that in which the condensation had taken place in the ortho position.

Conversion of the Benzoylbenzoic Acids into Anthraquinone Derivatives.—One part of each of the benzoylbenzoic acids was mixed with two parts of boric acid and dissolved in 15–20 parts of fuming sulfuric acid of a suitable concentration. The solutions were heated for varying times and at various temperatures and were then poured onto cracked ice. The resulting yellow precipitates were coagulated by warming and filtered off. The anthraquinone derivatives were purified by solution in 10% sodium carbonate, precipitation with carbon dioxide and crystallization from alcohol. All

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[8] Zahn and Ochwat, *Ann.*, **462**, 72 (1928).

[9] Barnett and Goodway, *J. Chem. Soc.*, 1754 (1929).

[10] Limpricht, *Ann.*, 314, 237 (1901).

[11] Scholl and Seer, *ibid.*, 394, 111 (1912).

[12] Ullmann and Schmidt, *Ber.*, 52, 2098 (1919).

formed yellow needles. The details are given in Table I. All of these compounds had been prepared previously and their properties agree with those given by previous investigators.

TABLE I

PREPARATIVE DATA

( )-Anthraquinone	% Excess SO_3	Temp., °C.	Time, minutes	Yield, %	M p , °C.
1-Hydroxy-	20	150	5	52	191–2.5[a]
1-Hydroxy-2-methyl-	10	100	5	62	184–5[b]
1-Hydroxy-3-methyl-	20	150	25	88	177–8[c]
1-Hydroxy-4-methyl-	0	100	30	72	174–5[d]

[a] Birukoff, *Ber.*, 20, 2438 (1887), and Ullmann and Conzetti, *ibid.*, 53, 828 (1920), give m. p. 193". [b] Bentley, Gardner and Weizmann, J. Chem. *Soc.*, **91**, 1626 (1907), Copisarow, *ibid.*, **117**, 209 (1920), and Keimatsu and Hirano, *Chem. Abstracts*, 23, 3464 (1929), give the same value. [c] Bentley, Gardner and Weizmann, ref. b, and Romer and Link, *Ber.*, 16, 700 (1883), give the same value. [d] Ullmann and Schmidt, *ibid.*, 52,2098 (1919), give 175°.

o-Benzylbenzoic Acids.—To a solution of one part of the benzoylbenzoic acid in three parts of water and 18–20 parts of concentrated ammonium hydroxide there was added three parts of zinc dust. The mixture was then heated gently for ten to twelve hours with mechanical stirring, ammonium hydroxide being added from time to time to maintain the concentration. The solution was filtered from the zinc and the *o*-benzylbenzoic acid precipitated by acidification with hydrochloric acid. The products were purified by solution in ammonium hydroxide, precipitation with hydrochloric acid and recrystallization from 50% methyl or ethyl alcohol, using decolorizing carbon, and from a mixture of benzene and petroleum ether. All of the acids were obtained as colorless needles. The yields and properties are given in Table II.

TABLE II

YIELDS AND PROPERTIES

a-( )-benzoic acid	M. p., °C.	Yield, %	Calcd., % C	Calcd., % H	Found, % C	Found, % H
(2-Hydroxyphenyl)-	133.8–4.5	98	73.66	5.30	73.31	5.09
(2-Hydroxy-3-methylbenzyl)-	158.2–159	85	74.36	5.83	74.11	5.60
(2-Hydroxy-4-methylbenzyl)-	1234	77.6	74.36	5.83	73.97	5.61
(2-Hydroxy-5-methylbenzyl)-	129–130	84.5	74.36	5.83	74.01	5.58

1-Hydroxy-9-anthrones.—To a solution of one part of the anthraquinone derivative in 40–50 parts of glacial acetic acid in a flask fitted with a reflux condenser there was added two to three parts of granulated tin. The solution was heated to boiling and three to four parts of concentrated hydrochloric acid was added in small portions during forty-five minutes. After the last addition of hydrochloric acid, the contents were boiled for an hour and then filtered while hot. Upon cooling, the filtrate deposited yellow needles of the anthrone. A further quantity was obtained by the addition of very dilute hydrochloric acid. The anthrones were purified by recrystallization from alcohol. The yields and properties are given in Table III.

1-Hydroxy-10-anthrone.—One part of the o-benzylbenzoic acid was dissolved in 20 parts of cold concentrated sulfuric acid and allowed to stand at room temperature for two hours, except that the preparation of 1-hydroxy-3-methyl-10-anthrone required fifteen hours. The resulting anthrones were precipitated by pouring the sulfuric acid solutions over cracked ice. They were purified by crystallization from alcohol and then

TABLE III

YIELDS AND PROPERTIES

			Calcd., %		Found, %	
-9-Anthrone	M. p., °C.	Yield, %	C	H	C	H
1-Hydroxy-	137.5–8[a]	89	...	..	...	..
1-Hydroxy-2-methyl-	136.2–7	94	80.47	5.39	80.59	5.54
1-Hydroxy-3-methyl-	158.2–9	85	80.47	5.39	80.38	5.19
1-Hydroxy-4-methyl-	167.4–8.2	94	80.47	5.39	80.11	5.13

[a] Liebermann and Mamlock, Ber.. 38, 1784 (1905), give 138"; Meyer and Sander, Ann., 420, 113 (1920), give 133–135°.

from a mixture of benzene and petroleum ether. All of the anthrones were colorless needles except 1-hydroxy-3-methyl-10-anthrone, which remained light tan in color after a number of recrystallizations. The yields and properties are given in Table IV.

TABLE IV

YIELDS AND PROPERTIES

			Calcd., %		Found, %	
-10-Anthrone	M. p. °C.	Yield, %	C	H	C	H
1-Hydroxy-	241–2[a]	82	79.97	4.80	79.69	4.65
1-Hydroxy-2-methyl-	207.2–8	93	80.47	5.39	80.10	5.20
1-Hydroxy-3-methyl-	258–9	66	80.47	5.39	79.99	5.11
1-Hydroxy-4-methyl-	226.2–7	97.5	80.47	5.39	80.25	5.22

[a] Cross and Perkin, J. Chem. *Soc.*, 306 (1930), give 240–242°.

Summary

1. The reduction of 1-hydroxyanthraquinone and its homologs yields only the corresponding 1-hydroxy-9-anthrone.

2. 1-Hydroxy-10-anthrone and its homologs can be obtained from suitable o-benzoylbenzoic acids by reduction to the corresponding *o*-benzylbenzoic acids and dehydration.

3. 1-Hydroxy-9-anthrone and its homologs are bright yellow, while 1-hydroxy-10-anthrone and its homologs are colorless, suggesting the possibility of benzenoid–quinoid tautomerism in the former case.

ST. LOUIS, MISSOURI

[CONTRIBUTION NO. 34 PROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OR UTAH]

ALPHA,BETA-DIPHENYLETHYL ETHER AND ALPHA-(PARA-METHOXYPHENYL-BETA-PHENYL)-ETHYL ETHER

BY CORLISS R. KINNEY AND W. GLEN BYWATER

RECEIVED JULY 7, 1930 PUBLISHED DECEMBER 18, 1930

In an attempt to oxidize the secondary alcohol, *p*-methoxyphenylbenzylcarbinol, with nitrogen trioxide, an unknown substance containing neither carbonyl groups nor nitrogen was obtained. Analyses and molecular weight determinations, as well as chemical properties, showed that the carbinol had been dehydrated to the corresponding ether, α-(*p*-methoxyphenyl)-β-phenylethyl ether. A similar reaction has been observed by a number of investigators,[1] who have shown that various acid reagents dehydrate diphenylcarbinol to its ether.

The new substance was also obtained in the preparation of *p*-methoxyphenylbenzylcarbinol, using the reaction of benzylmagnesium chloride with anisaldehyde.[2] The largest yields of the compound were obtained when the magnesium derivative was decomposed with a mixture of ice and concentrated hydrochloric acid. Following this procedure, no carbinol was isolated at all, and the major product was the dimolecular ether. Suspecting that dehydration of the carbinol was effected by the hydrochloric acid, several experiments were conducted using the pure carbinol, and varying ether–hydrochloric acid solutions. When the solution contained considerable acid, the carbinol was dehydrated to form *p*-methoxystilbene exclusively. Smaller concentrations of acid, however, in contact with anhydrous calcium chloride did give small amounts of the ether. The remainder of the carbinol was unchanged. The effect of the nitrogen trioxide gas, then, appeared to be that of an acid dehydrating agent similar to, but more effective than, hydrochloric acid. The larger yield of the ether from the Grignard reaction indicated that the dehydration occurred during the reaction or the process of decomposition of the magnesium derivative with the acid rather than a subsequent dehydration of the carbinol in an acidic ether extract.

Phenylbenzylcarbinol was transformed into its ether with somewhat greater difficulty than the methoxyl derivative. The method using nitrogen trioxide was not nearly as effective, nor was any ether isolated from the product of the reaction of benzylmagnesium chloride with benzalde-

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[1] (a) Linnemann, *Ann.*, **133**, 6 (1864); (b) Zagumenny, *ibid.*, **184**, 174 (1876); (c) Hofmann, Roth, Höbold and Metzler, *Ber.*, **43**, 2629 (1910); (d) Adams and Weeks, THIS JOURNAL, **38**, 2516 (1916); (e) Szperl and Wierusz-Kowalski, *Chem. Polski*, 15, *23* (1917). *Chem. Abst.*, **13**, 2865 (1919).

[2] The ether of diphenylcarbinol was also obtained, among other products, by Oddo, *Gazz. chim. ital., 111]* **37**, 356–66 (1907), from bromobenzene, magnesium, pyridine and benzaldehyde.

hyde. Small quantities of the ether were obtained, however, by the action of hydrochloric acid in an ether solution of the carbinol in contact with anhydrous calcium chloride.

Experimental Part

Preparation of **α-(*p*-Methoxyphenyl)-β-phenylethyl** Ether. (a) By the Action of Nitrogen **Trioxide** on ***p*-Methoxyphenylbenzylcarbinol.**—Thirty grams of pure *p*-methoxyphenylbenzylcarbinol was dissolved in 100 cc. of absolute ether and a slow stream of nitrogen trioxide from arsenic trioxide and nitric acid (sp. gr. 1.3) passed through the solution for twenty hours. The solid that crystallized out weighed nearly 8 g. and melted at 140–145°.

(b) Preparation of the Ether in the Reaction of **Benzylmagnesium** Chloride with Anisaldehyde.—The reaction of benzylmagnesium chloride with anisaldehyde normally gave yields of 64% of p-methoxyphenylbenzylcarbinol melting at 53–56" when the reaction mixture was carefully poured on ice and the precipitated basic magnesium salts dissolved with dilute sulfuric acid. None of the ether was isolated in such experiments. However, when the reaction mixture was poured into cracked ice and concentrated hydrochloric acid, the dimolecular ether separated from the solution, in which it was only slightly soluble, in large amounts. The oily residue failed to yield any of the carbinol, which is low melting.

(c) Preparation by the Action of Hydrochloric Acid.—Dry hydrogen chloride was passed into an absolute ether solution of 4 g. of p-methoxyphenylbenzylcarbinol for one hour. The carbinol was largely dehydrated to p-methoxystilbene, as proved by a mixed melting point determination. The yield was 2.54 g. or 69%.

Two grams of the carbinol and 2 cc. of concentrated hydrochloric acid were dissolved in about 40 cc. of ether and allowed to stand over calcium chloride (anhydrous) for several hours. As before, the carbinol was changed into p-methoxystilbene. The yield was 1.1 g. or 60%.

Finally 0.77 g. and 0.73 g. were allowed to stand over calcium chloride (anhydrous) in ether solutions containing one and two drops of concentrated hydrochloric acid, respectively. The first yielded 0.05 g. of the ether and the second 0.03 g. The remainder of the carbinol was recovered practically quantitatively.

Properties and Analyses of **α(*p*-Methoxyphenyl)-β-phenylethyl** Ether.—The ether was best purified by solution in a small amount of chloroform followed by dilution with several volumes of hot methyl alcohol. It crystallized in needles of m. p. 148–149° (uncorr.), was readily soluble in chloroform, moderately in acetone, slightly soluble in ether or alcohol and insoluble in petroleum ether.

Anal.[3] Subs., 0.2409, 0.2886: CO_2, 0.7274, 0.8643; H_2O, 0.1531, 0.1770. Calcd. for $C_{30}H_{30}O_3$: C, 82.19; H, 6.82. Found: C, 82.35, 81.96; H, 7.11, 6.86.

Mol. wt.: Calcd. for $C_{30}H_{30}O_3$: 438. Found: in chloroform, subs., 1.3866, 1.567; wt. of chloroform, 77.61; b. p. elevation, 0.200, 0.205"; mol. wt. 326.5, 368. Mol. wt. in camphor: subs., 0.0198, 0.0277, 0.3092; m. p. depression, 6.5, 6.9"; mol. wt., 393, 425.

The ether did not react with phenylhydrazine, hydroxylamine, sodium bisulfite, Schiff's reagent, sodium metal, nor benzoyl chloride. When boiled with hydrogen iodide in a Zeisel apparatus methyl iodide was produced, showing that the methoxyl group had not entered into a reaction. Oxidation with chromic anhydride in glacial acetic acid yielded benzoic and anisic acids. Distillation yielded a new substance melting at 107–108°, which was not p-methoxystilbene, m. p. 136°. Bromination with

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[3] Analysis made by Mr. D. P. Langlois of this Laboratory.

evolution of hydrogen bromide yielded a bromide melting at 174–175°. The bromide was not the dibromide of *p*-methoxystilbene, m. p. 177°.

Preparation of α,β-**Diphenylethyl** Ether. (a) **By** the Action of Nitrogen **Trioxide.**—Seven grams of phenylbenzylcarbinol was dissolved in dry ether and nitrogen trioxide, obtained as before, passed into the solution overnight. The ether was evaporated and the residue extracted with methyl alcohol, which dissolved the unchanged carbinol, leaving **0.5** g. of a substance melting at 129–130°.

Several other experiments, in which dry nitrogen trioxide was used, failed to produce the compound.

(b) **By** the Action of Hydrochloric Acid.—Three grams of phenylbenzylcarbinol was dissolved in ether and 4 cc of concentrated hydrochloric acid and anhydrous calcium chloride were added. The mixture was allowed to stand for one hour and then refluxed for an hour. More anhydrous calcium chloride was added and the flask set aside for three and one-half days. The ether solution was filtered and evaporated. The residue was dissolved in hot methyl alcohol, and on cooling **1.95** g. of slightly impure carbinol crystallized out. This material was extracted with a small amount of methyl alcohol, which left **0.135** g. of ether melting at 123–127°.

Properties **and** Analyses of α,β-**Diphenyl** Ethyl Ether.—The ether was purified by recrystallization from boiling methyl alcohol. It crystallized in needles, m. p. 129.5–130.5° (uncorr.), was readily soluble in chloroform, slightly soluble in ether or alcohol and insoluble in petroleum ether.

Anal.[4] Subs., **0.0512:** CO_2, **0.1675;** H_2O, **0.0322.** Calcd. for $C_{28}H_{26}O$: C, 88.88; H, 6.87. Found: C, 89.21; H, 7.04.

Mol. wt.: Calcd. for $C_{28}H_{26}O$: mol. wt., **378.** Mol. wt. in camphor: subs., **0.0031;** wt. of camphor, **0.0478;** depression of melting point, 6.4°. Mol. wt. found: **383.8.**

Summary

p-Methoxyphenylbenzylcarbinol and phenylbenzylcarbinol have been found to be dehydrated to their ethers under certain acidic conditions.

SALT LAKE CITY, UTAH

[CONTRIBUTION FROM THE ROCKEFELLER PHYSICAL LABORATORY AND THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

THE ABSORPTION SPECTRA OF THE GAMMA-PYRONES AND PYROXONIUM SALTS[1]

BY R. C. GIBBS, JOHN R. JOHNSON AND E. C. HUGHES[2]

RECEIVED JULY 15, 1930 PUBLISHED DECEMBER 18, 1930

The unusual properties of the pyrone ring have resulted in considerable speculation concerning its structure. Investigations of the physical and chemical properties of the compounds in this group have led to the formulation of several different structures for the nucleus, none of which has been firmly established or generally accepted.

[4] Analysis made by Mr. Berne Woolley of this Laboratory.

[1] The investigations upon which this article is based were supported by grants from the Heckscher Foundation for the Advancement of Research, established at Cornell University by August Heckscher.

[2] Heckscher Research Assistant in Chemistry and Physics at Cornell University, **1928–1930.**

Qualitative investigations of the ultraviolet absorption spectra of γ-pyrone, y-dimethylpyrone, some of their derivatives and their salts have been reported.[3] Xanthene and xanthone have been studied in relation to the flavones.[4] The absorption of chelidonic acid and pyrone have been examined quantitatively by Riegel and Reinhard.[5]

It has been suggested as a result of a number of investigations from different angles of attack that the products of the action of acids upon the pyrones are oxonium compounds.[6]

In order to clarify the problem we have made a quantitative study of the series: y-pyrone, y-benzopyrone (chromone) and xanthone, and some of their derivatives. The investigation of the ultraviolet absorption spectra has been made with the Hilger sectorphotometer method as employed by Orndorff, Gibbs and McNulty.[7] The cells used were 0.331 cm. and 1.00 cm. thick. Beer's law was found to hold for all of the solutions over the range of concentrations indicated in the legends on the graphs. The molecular absorption coefficient is represented by ϵ.

The spectra of the following compounds were examined in absolute alcohol and alcoholic hydrogen chloride: pyrone (Fig. 1, A and B), dimethylpyrone (Fig. 1, E and F), benzopyrone, (Fig. 2, D and E) and xanthone (Fig. 2, A and B). Since there is a partial dissociation of the hydrochloride of dimethylpyrone in ionizing solvents, the absorption was also measured in an ether solution of hydrogen chloride. Xanthone and dimethylpyrone were also examined in sulfuric acid. The compound of dimethylpyrone with dimethyl sulfate, which has been shown to be an oxonium compound[Z1] was examined in alcohol (Fig. 3, D) and, to obviate any effects due to dissociation, in pure dimethyl sulfate (Fig. 3, E). The curves for the acid solutions of each of these compounds resemble those for the neutral solutions, except that the bands are shifted slightly toward the red. It is evident, therefore, that the formation of oxonium complexes produces no profound change in the structure of the ring.

A possible objection which might be raised to the above conclusion is that Kendall[6e] has stated that the compounds of dimethylpyrone with numerous organic acids are colored. We have found that these compounds, when made from dimethylpyrone which had been sublimed and recrystal-

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[3] (a) Baly, Collie and Watson, *J. Chem. Soc.*, 95, 144 (1909); (b) Boon, Wilson and Heilbron, ibid., 105, 2176 (1914); (c) Hantzsch, *Ber.*, 52, 1535 (1919).

[4] Tasaki, *Acta Phytochim.*, 3, 1 (1927); C. A., 22, 1591 (1928).

[5] Riegel and Reinhard, THIS JOURNAL, 48, 1334 (1926).

[6] (a) Collie and Tickle, *J. Chem. Soc.*, 75, 710 (1899); (b) Walden, *Ber.*, 34, 4185 (1901); (c) Baeyer, *ibid.*. 43,2337 (1910); (d) McIntosh, THIS JOURNAL, 32, 542 (1910); (e) Kendall, *ibid.*, 36, 1222 (1914); (f) Rördam, *ibid.*, 37, 557 (1915); (g) Gomberg and Cone, *Ann.*, 376, 183 (1910). The last-named investigators are, however, opposed to the view that these salts are oxonium compounds.

[7] Orndorff, Gibbs and McNulty, THIS JOURNAL, 47, 2767 (1925).

lized, are *colorless.* When a sample of Kahlbaum's dimethylpyrone was used without purification, as Kendall did, colored compounds were produced.

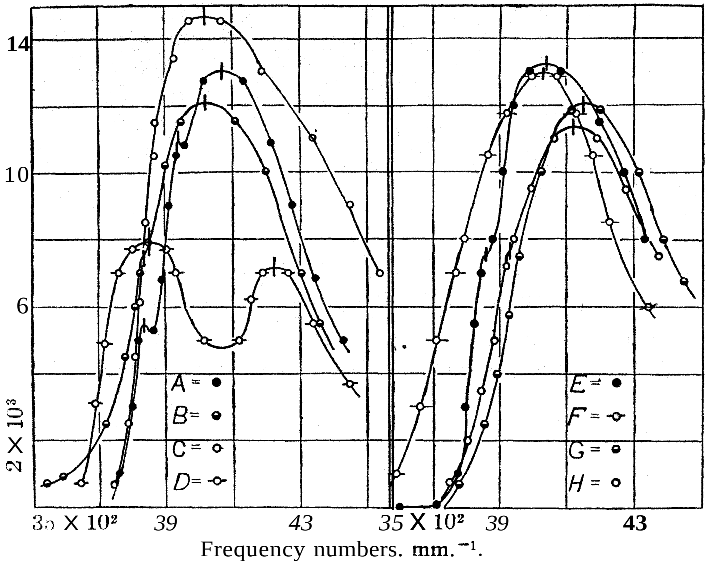

Fig. 1.—Pyrone: A, in alcohol (concn., 0.0002 to 0.00033 molar); B, same plus 5000 moles of HCl (concn., 0.0003 to 0.0005 molar). Dimethylpyrone: C, in water; D, in concd. sulfuric acid; E, in absolute alcohol, or the same plus 200 moles of sodium ethoxide; F, in absolute alcohol plus 300 moles of HCl; G, in anhydrous ether; H, same plus 2500 moles of HCl. The concentration range used in E, F, G and H was 0.0002 to 0.007 molar.

These observations lead to the conclusion that the structure of the nucleus of the pyrone ring is the same in the free pyrone as in the pyroxonium compounds. This is analogous to the similarity of the absorption spectra of the amines and the corresponding ammonium compounds.[8]

The earliest formula suggested for the pyrones is the ketone form, I, and the salts were considered to be the result of the addition of acid to either of the two oxygen atoms, II*a* and b. From a study of the absorption spectra Hantzsch[c] made the suggestion that the salts were of the coördination type as shown in III. It was then suggested by other investigator that an inner salt formula, IV*a*, would explain the anomalous properties of the pyrones. This formula is a modern conception of the formula IV*b* suggested by Baly[3a] in 1909. It is to be noted that the inner salt formula has a nucleus which is benzenoid and that the ketonic formula

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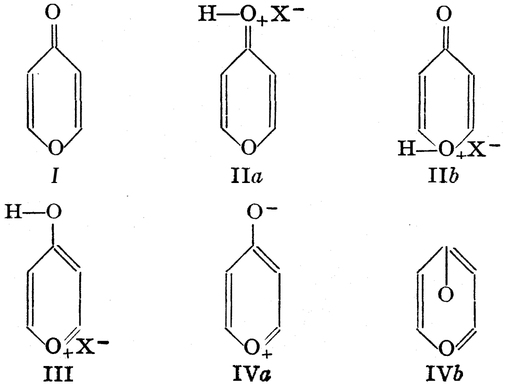
[8] Hartley, J. Chem. *Soc.*, **47,** 685 (1885); Baker and Raly, *ibid.*, 91, 1122 (1907); Hantzsch, *Ber.*, 44, 1783 (1911).

[9] Heilbron, Barnes and Morton, J. *Chem. Soc.*, 123, 2659 (1923).



FORMULAS OF PYRONE AND PYROXONIUM SALTS

has a structure which is analogous to the quinoid structure in the benzene series. Heilbron, Barnes and Morton[5] suggest the possibility of an equilibrium existing between the two forms. Since the shift from the quinoid to the benzenoid type of structure always produces a marked change in

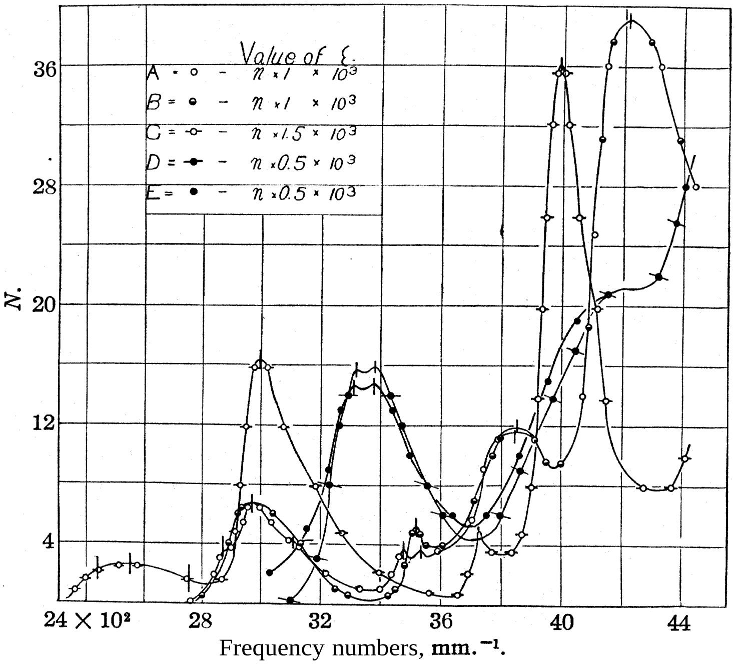


Fig. 2.—Xanthone: A, in absolute alcohol; B, same plus 5000 moles HCl; C, in concd. sulfuric acid. The concentration range used in A, B and C was 0.00003 to 0.005 molar. Benzopyrone: D, in absolute alcohol; E, the same plus 5000 moles HCl. The concentration range in D and E was 0.00005 to 0.005 molar.

the absorption spectrum, such an equilibrium could be detected by this method.

However, the absorption spectrum of dimethylpyrone in neutral alcohol is identical with that in alkaline alcohol (Fig. 1, E), and very similar to that in alcoholic hydrogen chloride (Fig. 1, F). This indicates that the pyrones do not exist in such an equilibrium in solution. Baly[3a] has reported a considerable difference between the absorption spectra in neutral and alkaline solutions. However, water was present in his solutions and it is known that the pyrone ring is unstable in the presence of aqueous alkali. In our measurements, on the other hand, absolute alcohol was used as the solvent.

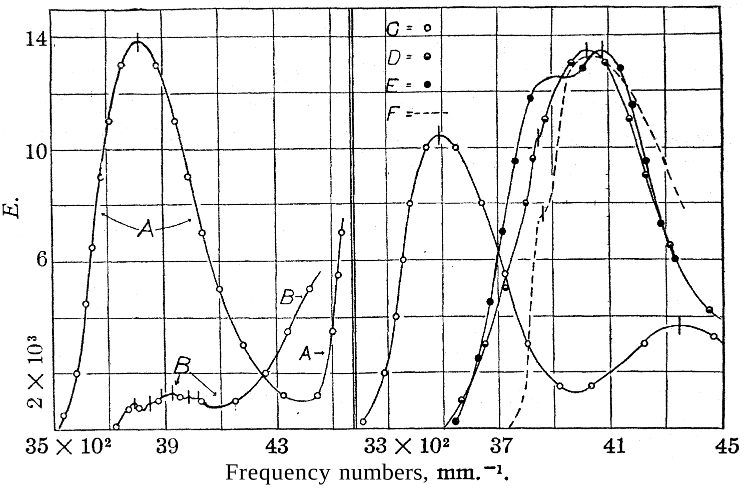
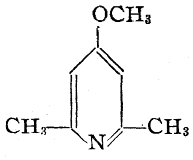
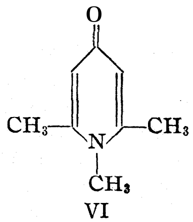


Fig. 3.—A, 1,2,6-Trimethyl-4-pyridone, in absolute alcohol (concn., 0.00035 to 0.004 molar); B, 4-methoxy-2,6-dimethylpyridine, in absolute alcohol (concn., 0.0007 to 0.004 molar); C, 2,4,6-trimethylpyroxonium perchlorate in alcohol (concn., 0.0004 to 0.0015 molar); D, dimethylpyrone + dimethyl sulfate in alcohol; E, dimethylpyrone in pure dimethyl sulfate (concn. of D and E, 0.0002 to 0.0017 molar); F, dimethylpyrone, see Fig. 1.

To obtain further information as an aid in deciding among the proposed structures, the product of the action of aqueous ammonia upon the oxonium complex of dimethylpyrone and dimethyl sulfate was studied. This reaction yields 4-methoxy-2,6-dimethylpyridine, V, a compound in which





VI

only the benzenoid structure is possible. The absorption spectrum of this substance is compared with that of its ketonic isomer, 1,2,6-trimethyl-4-pyridone, VI (Fig. 3, A and B). This comparison illustrates the great change in character and intensity of absorption that occurs upon transition from the benzenoid to the quinoid type of structure. The spectrum of the pyridone derivative bears a close resemblance to that of pyrone, but that of the pyridine derivative does not. This indicates that the pyrones and salts correspond to the ketonic formula. Evidently, as a result of the treatment with ammonium carbonate, the cyclic nucleus of dimethylpyrone has undergone a rearrangement. Since the product of this action is 4-methoxy-2,6-dimethylpyridine, it is assumed that the oxonium compounds are formed through the residual valences of the ketonic oxygen and not those of the ether oxygen. This assumption is supported by several investigators using different methods of study.[10] The free pyrone compounds would therefore be best represented by the ketonic structure I and the salts of the pyrones by the oxonium type of structure, II*a*.[11]

Xanthene and xanthydrol are known to have a quinoid type structure and have been examined in comparison with the absorption spectra of xanthone (Fig. 4, A and B). To illustrate the similarity between the absorption spectra of these three compounds, the frequencies of their maxima have been arranged in Table I.

TABLE I

ABSORPTION MAXIMA IN MM.$^{-1}$

Xanthone	2965	3470	3533	3850	4216
Xanthene		3425	3538		4050
Xanthydrol		3445	3533		4215

This would indicate that the pyrone group in xanthone is similar to the central portion of the molecule in xanthene and xanthydrol, that is, quinoid in structure.

In order to establish that the structure of pyrone and its derivatives is of the quinoid type, it would be desirable to show that analogous compounds, in which the structure is known to be of the benzenoid type, exhibit entirely different absorption spectra. The compounds resulting from the

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[10] Maass and McIntosh, THIS JOURNAL, 34, 1273 (1912); Kendall and Carpenter. *ibid.*, 36, 2498 (1914); Tschelinzeff, *Bull. soc. chim.*, [4] 35, 741 (1924). The above statement should not be construed to mean that it is impossible for the ring oxygen to form an oxonium compound. The evidence is simply that the formation of oxonium compounds occurs with much greater ease through the ketonic oxygen, and that such oxonium compounds are much more stable than those derived from ethers.

[11] This would explain the failure of the attempts by Gibson and Simonsen [*J. Chem. Soc.*, 2307 (1928)] to resolve derivatives of pyrone in the form of salts. They conclude that their failure indicates that the salts have the coordination formula, III, but the attachment of the acid to the ketonic oxygen would also preclude the possibility of a resolution.

action of acids on xanthydrol have been formulated as oxonium compounds having a benzenoid structure[12] and should therefore show very different absorption spectra from those of xanthydrol, xanthene and xanthone in a neutral solvent. Trimethylpyroxonium perchlorate has also been formulated as being an oxonium compound of benzenoid structure.[13] A comparison of the absorption spectra of these oxonium salts with their pyrone analogs would possibly furnish information concerning the structure of the latter. However, the spectrum of xanthydrol in absolute alcoholic hydrogen chloride is identical with xanthene in neutral and acid solvents (Fig. 4, B). This indicates that the hydroxyl group has been directly replaced by chlorine without any profound change in the molecular structure. On the other hand, in concentrated sulfuric acid and in aqueous hydrochloric acid, xanthydrol exhibits an entirely different spectrum (Fig. 4, C).

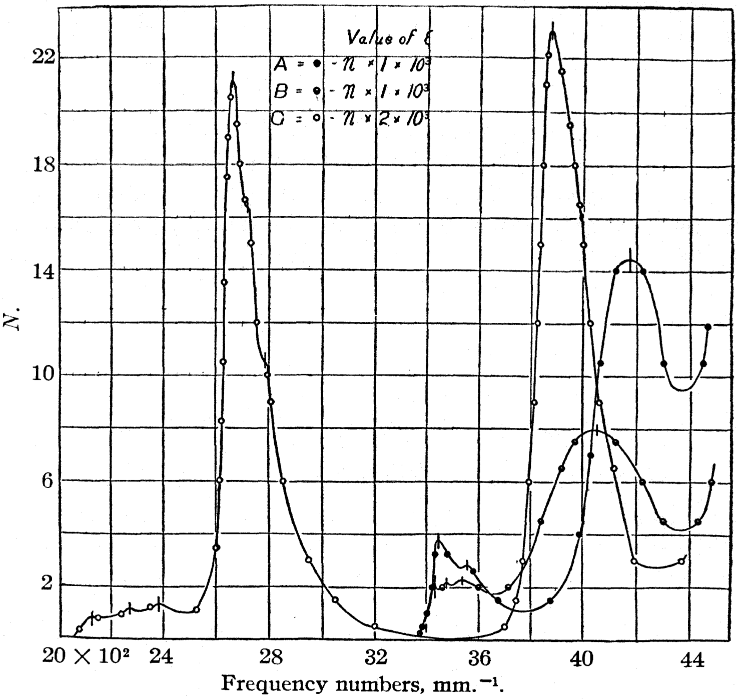

Fig. 4.—A, Xanthydrol in absolute alcohol (concn., 0.00025 to 0.001 molar); B, xanthene in alcohol, coincides with xanthene in 4 *N* alcoholic HCl and with xanthydrol in 4 *N* alcoholic HCl (concn. in all three cases, 0.00035 to 0.0017 molar); C, xanthydrol in concd. sulfuric acid (concn. 0.00008 to 0.005 molar).

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[12] Werner, Ber., 34, 3301 (1901).

[13] Baeyer and Piccard, Ann., 384, 208 (1911); 407, 332 (1915). Hantzsch, Kef. 3c, reported the absorption spectra of this compound qualitatively.

This would indicate that the replacement or reaction of the hydroxyl group has been accompanied by a rearrangement of the cyclic nucleus.

Although the spectra of xanthydrol in the acid media differ greatly from those of xanthone, it would not be justifiable to draw conclusions as to the structure of the latter. There is considerable chemical evidence that the structure of the xanthydrol–acid complexes is not of the oxonium type.[14] The absorption spectra of fluoran[15] and of xanthene[16] in concentrated sulfuric acid are practically identical with that of xanthydrol in the same solvent. These two cannot rearrange in the way postulated for the formation of the oxonium compound of xanthydrol, without rupturing the molecule. The possibility is then indicated that the structure of these is not that of an oxonium compound. This would apply also to trimethylpyroxonium perchlorate, the spectrum of which is shown in comparison to that of dimethylpyrone (Fig. 3). If the structure is benzenoid, it should differ much more markedly from the spectrum of dimethylpyrone than it does. Hantzsch[3c] bases his deductions as to the structure of the pyrone salts upon the similarity of the spectra of these two series of salts. In the light of the above observations such a deduction is not justifiable until the structure of the perchlorate has been more firmly established.

The authors wish to acknowledge their indebtedness to Dr. C. V. Shapiro for many helpful suggestions during the course of this investigation.

Materials

The compounds used in this investigation were prepared and purified by the following methods; no particular care was given to the yield but only to the purity of the product. In the spectroscopical examination, two different samples were always used to aid in the detection of effects due to the possible presence of impurities. All melting points given are corrected.

Pyrone was prepared by the decarboxylation of chelidonic acid as described by Wiilstatter and Pummerer[17] and was purified by several fractionations under reduced pressure; b. p. 88.5° (7 mm.), m. p. 32.5°.

Dimethylpyrone was obtained from Kahlbaum, m. p. 132° before further purification. It was sublimed at 100° and twice recrystallized from redistilled ether; m. p. 132.1°.[18]

Benzopyrone (chromone) was prepared by the method of Ruhemann and that of Gomberg and Cone.[19] It was redistilled under reduced pressure and recrystallized from petroleum ether (boiling point, 70–80°). The melting point was 56° in accordance with Gomberg and Cone; Ruhemann gives 59°.

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[14] Gomberg and Cone, Ref. 6g and *Ann.*, 370, 152 (1909).

[15] Orndorff, Gibbs and Shapiro, THIS JOURNAL, 50, 819 (1928).

[16] Unpublished data.

[17] Willstätter and Pummerer, *Be?.*, 37, 3733 (1904).

[18] Collie, J. Chem. *Soc.*, 59, 619 (1891).

[19] Ruhemann, *ibid.*, 77, 984, 1123, 1184 (1900); Heywang and Kostanecki, *Ber.*, 35, 2887 (1902); Gomberg and Cone, *Ann.*, 376, 228 (1910).

Xanthone was prepared according to the directions of Holleman[20] and was recrystallized four times from 95% alcohol. A sample obtained from Kahlbaum was also purified and examined. Both samples melted at 174°.

4-Methoxy-2,6-dimethylpyridine was prepared from purified dimethylpyrone by forming trimethylpyroxonium perchlorate (m. p. 192–193°, with dec.), and treating this with a cold solution of ammonium carbonate. It was redistilled under reduced pressure; b. p. 99–100° (21 mm.); 203.5° (748 mm.); d_{16}^{24} 1.015.[21] The refractive index of the first and last drops of the fraction used was n_D^{20} 1.5082.

1,2,6-Trimethyl-4-pyridone was prepared from the above methoxylutidine by treatment of the methiodide with freshly precipitated silver oxide. It was crystallized twice from water and once from chloroform, and dried for two days at 140° under reduced pressure; m. p. 245°.[22]

Trimethylpyroxonium perchlorate was prepared by hydrolysis with perchloric acid of the product of the reaction between dimethylpyrone and methylmagnesium bromide. It was four times recrystallized from ethyl alcohol and from water; m. p. 242–245°.[23]

Xanthene was obtained by the reduction of purified xanthone with sodium in alcohol.[24] It was steam distilled and recrystallized twice from alcohol and dried at 50°; m. p. 101°. Examination of the absorption spectrum showed that it contained no xanthone.

Xanthydrol was made by the reduction of xanthone with sodium amalgam.[25] It was twice recrystallized from alcohol without heating the solution in order to prevent the formation of dixanthyl ether. It was dried under reduced pressure over sulfuric acid for three hours and used immediately; m. p. 123–124°.[26]

Absolute alcohol was obtained from the United States Industrial Alcohol Corporation and carefully redistilled before use. In special cases when particularly anhydrous conditions were required, this product was dried over calcium oxide.

Dimethyl sulfate was obtained from Kahlbaum and was dried and distilled under diminished pressure over barium oxide in an all glass apparatus. It did not give a test for free acid and was transparent to 2200 Å.

Summary

It has been observed that the ultraviolet absorption spectra of γ-pyrone, dimethylpyrone, benzopyrone and xanthone in acid solution are very similar to the spectra in neutral solution. These data lead to the conclusion that the formation of oxonium compounds in this series does not result in any profound change in the structure of the molecule.

The identity of the absorption spectra curves of dimethylpyrone in neutral and alkaline media, and their similarity to the curve in acid solution precludes the possibility of an equilibrium existing between two different types of structure of the ring

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[20] "Organic Syntheses," John Wiley and Sons, New York, 1927, Vol. VII, p. 84.

[21] Baeyer, *Ber.*, 43, 2337 (1910); Baeyer and Piccard, *Ann.*, 407, 337 (1914).

[22] Conrad and Eckhardt, *Ber.*, 22, 81 (1889); Michaelis and Hanisch, *ibid.*, 35, 3158 (1902).

[23] Baeyer and Piccard, *Ann.*, 384, 215 (1911).

[24] Heller and Kostanecki, *Ber.*, 41, 1325 (1908).

[25] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1927, Vol. VII, p. 88.

[26] Meyer and Saul, *Ber.*, 26, 1276 (1893).

A resemblance between the absorption spectra of dimethylpyrone (and its salts) and 1,2,6-trimethylpyridone, a compound in which only the ketone structure is possible, and between those of xanthone and of xanthene and xanthydrol has been observed. On the other hand, it has been noted that the spectrum of dimethylpyrone differs greatly from that of 4-methoxy-2,6-dimethylpyridine, an analogous compound which has the benzenoid type of structure.' From these observations the conclusion has been drawn that the structure of the pyrone and pyroxonium ring is best represented by a ketonic formula.

It has been pointed out that formulation of the salts of xanthydrol and of trimethylpyroxonium perchlorate as compounds of an oxonium type is open to question.

ITHACA, NEW YORK

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

ELECTROLYSIS OF GRIGNARD SOLUTIONS[1]

BY H. E. FRENCH AND MARY DRANE

RECEIVED JULY 22, 1930 PUBLISHED DECEMBER 18, 1930

In a previous article[2] there is described a series of experiments on the electrolysis of certain Grignard compounds in ether solutions, using platinum electrodes. The purpose of that investigation was to determine the quantity of a Grignard compound which is decomposed by one equivalent of electricity, and to determine the products resulting from that decomposition.

The present paper describes some experiments on the electrolysis of Grignard solutions using anodes of various metals with platinum cathodes.

Apparatus and Procedure

The electrolytic cells were made of glass tubing, and were approximately 200 X 40 mm. in size. These were closed with tight fitting cork stoppers through which the two electrodes were suspended close to the stoppers by copper wires. These electrodes were held parallel to each other and about 3 cm. apart by means of bent glass rods. Short-circuiting between the electrodes through the formation of bushy deposits of magnesium on the cathode was prevented by placing on the bottom of each cell a long glass rod with which such deposits were broken off by occasionally tilting the cell.

A glass tube of 1 cm. diameter was inserted through the center of each of the stoppers which closed the cells, and extended about 1 cm. beyond the inner faces of the stoppers. Through these tubes the cells were filled and emptied.

For anode materials the following metals were used, either in the form of the foil or as long narrow flat pieces of the metal: aluminum, tin, cadmium, zinc, bismuth, gold, silver and nickel. The areas of the anodes were approximately 20 sq. cm., while those of the platinum cathodes were about 10 sq. cm. In order to eliminate the magnesium

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[1] This paper is an abstract of the thesis submitted by Mary Drane in partial fulfilment of the requirements for the degree of Master of Arts at the University of Missouri.

[2] Gaddum and French, THIS JOURNAL, 49, 1295 (1927).

halide etherates as factors in the electrolyses, isoamylmagnesium chloride was chosen for these experiments, the magnesium chloride etherate being but slightly soluble in the ether.

The currents through the solutions varied from 24 to 100 milliamperes, under a potential of 110 volts. Since this caused the solutions to boil vigorously, the currents were adjusted to 10 milliamperes for the first fifty hours and to 20 milliamperes for the remaining one hundred and fifty hours, by the introduction of resistances. In every case a light, bushy deposit of magnesium began to form on the cathode within a few minutes after starting the electrolysis.

When the electrolysis was complete, the solutions were drawn from the cells by suction and filtered, and both the filtrates and the residues were analyzed for the anode material. The concentration of the Grignard compound was also determined, before and after the electrolysis The results are summarized in Table I.

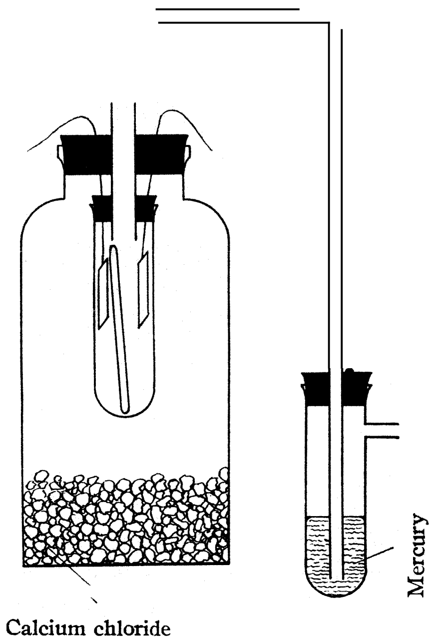

Fig. 1.

Of the various anodes, only the aluminum, zinc and cadmium were attacked during the course of the electrolysis. Of these metals, only the aluminum was found in the ether solution, presumably in the form of the aluminum alkyl. In this cell the conductance was apparently due to the magnesium compound alone, since all of the aluminum was found in the solution, and was approximately equivalent to the quantity of electricity passing through the cell. The appearance of the zinc and cadmium anodes in the earlier experiments led us to suspect that small pieces might have broken off and fallen to the bottom of the cells. Those results were therefore discarded, and the experiments were repeated using paper extraction thimbles around the anodes.

TABLE I

SUMMARY OF ELECTROLYSIS EXPERIMENTS

Cell	Anode material	Molar concn. of Grignard compound	Equiv. of Grignard compound in the cell At start	At end	Change	Equiv of anode material found In soln.	In residue	Coulometer reading in equiv.
1	Aluminum	2.231	0.383	0.104	0.279	0.074	0.000	0.082
2	Bismuth	1 692	.338	286	.052	.000	.000	.052
3	Gold	1.682	.321	260	.060	.000	.000	.063
4	Nickel	2.231	.629	490	.138	.000	.000	.104
5	Silver	2.231	.334	218	.116	.000	.000	.117
6	Tin	2.231	.334	.254	.079	.000	.000	.099
7	Zinc	1.647	288	.211	.077	000	.044	.071
8	Cadmium	1.647	288	.254	.034	.000	.022	.031

In both of these cases anode material dissolved off and was found later in the residue in the bottom of the cell, while the ether solutions contained none of that material. In neither case was the amount of anode material which was recovered equivalent to the amount of current passing through the solution. Presumably, in these two cells, the anode materials formed metallic alkyls as the result of electrolytic action and were then decomposed by the electric current simultaneously with the Grignard compound. Cadmium alkyls, however, have been reported as being decomposed by the action of light, with the deposition of metallic cadmium[3] and it is possible that the cadmium obtained in these experiments was formed, in part at least, by such action.

In Cells 2, 3 and 5 the amount of isoamylmagnesium chloride decomposed was equivalent, within experimental error, to the quantity of current passing through the solutions. In Cells 1, 4, 7 and 8 the amount of chemical change was greater than can be accounted for by the quantity of current carried. This failure of the analytical results to check is readily explained by the fact that in these cells a certain amount of hydrolysis took place with the formation of a precipitate of basic magnesium chloride. In cell No. 6, however, the amount of chemical change was less than would have been expected on the basis of the quantity of electricity carried through the cell. It is possible that this was due to a short circuit between the electrodes formed by a deposit of magnesium along the glass rod used to hold the electrodes in place. Such a deposit might have escaped observation, since the solution was dark colored.

Summary

1. Ether solutions of isoamylmagnesium chloride were subjected to electrolysis using anodes of various metals and cathodes of platinum.

2. Anodes of aluminum, zinc and cadmium were dissolved off as the result of electrolytic action. Those of bismuth, gold, nickel, silver and tin were not attacked. The amount of aluminum which went into solution was approximately equivalent to the quantity of current passing through the cell.

3. In several cases where the anode was not attacked, an amount of isoamylmagnesium chloride equivalent to the amount of current passing through the cell was decomposed.

COLUMBIA, MISSOURI

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[3] J. Newton Friend, "Textbook of Inorganic Chemistry," Vol. XI, p. 27.

[Contribution from the Soil Fertility Laboratory, Bureau of Chemistry and Soils, U. S. Department of Agriculture]

THE PRESENCE OF URONIC ACIDS IN SOILS

By E. C. Shorey and J. B. Martin

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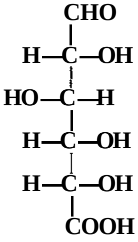
Uronic acids, represented by glucuronic and the isomeric galacturonic acids, while not often found free in natural products, are abundant in plant and animal tissues as part of complex bodies, frequently spoken of as polyuronides. As such they are found in some hemicelluloses, in pectin, and in the glycoproteins of animal tissues and apparently in some of the "slime" products of micro-organisms.

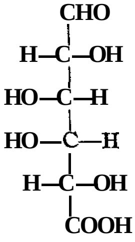
Such plant and animal tissues, of course, find their way into soils and complex compounds containing uronic acid nuclei might be expected to form some part of the organic matter of soils.

Uronic acids are represented by the formula $C_6H_{10}O_7$ and structurally



$$\begin{array}{c} \text{CHO} \\ | \\ \text{H—C—OH} \\ | \\ \text{HO—C—H} \\ | \\ \text{H—C—OH} \\ | \\ \text{H—C—OH} \\ | \\ \text{COOH} \end{array}$$

d-Glucuronic



$$\begin{array}{c} \text{CHO} \\ | \\ \text{H—C—OH} \\ | \\ \text{HO—C—H} \\ | \\ \text{HO—C—H} \\ | \\ \text{H—C—OH} \\ | \\ \text{COOH} \end{array}$$

d-Galacturonic

These acids are characterized by being rather easily decarboxylated by heating with strong acid, each molecule losing one molecule of carbon dioxide, being thereby converted into the corresponding pentose sugar

$$C_6H_{10}O_7 = C_5H_{10}O_5 + CO_2$$

d-Glucuronic acid by this process—boiling with 12% hydrochloric acid—gives d-xylose, while d-galacturonic acid gives *l*-arabinose.

Each of these sugars, when boiled with 12% hydrochloric acid for liberation of carbon dioxide, breaks down further to give furfural and water

$$C_5H_{10}O_5 = C_5H_4O_2 + 3H_2O$$

so that under this treatment there is evolution of carbon dioxide and formation of furfural at the same time.

It has been known for some time that practically all soils when boiled with 12% hydrochloric acid give furfural, the quantity of which can be determined in the usual way by precipitation as the phloroglucide. Shorey and Lathrop[1] showed that in ten soils of quite widely differing types the furfural obtained calculated to pentosan, varied from 0.055 to 2.75%—in one case representing 28.5% of the total carbon in the soil. Lathrop[2]

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[1] Shorey and Lathrop, This Journal, 32,1680 (1910).

[2] Lathrop, unpublished data.

found in nine soils—clays and loams—the furfural calculated to pentosan varied from 0.181 to 0.598% and in sixteen peats varied from 0.50% in the peat from Lake Mattamuskete, North Carolina, to 5.25% on a brown fibrous peat from the Florida Everglades (mile post 39).

Heretofore the formation of furfural when a soil is boiled with 12% hydrochloric acid, has been ascribed to the presence of pentosans, represented in plant tissues by that somewhat indefinite group of compounds known as hemicelluloses, and assumed to be in soils as plant residues. In fact, such a pentosan was isolated from a sample of Marshall loam from North Dakota, a soil containing 6.97% organic carbon.[3]

However, it may be assumed that furfural from soils might be derived from any plant or animal constituent known to give rise to furfural and not necessarily from a pentosan.

A method for determining uronic acids based on a measurement of the carbon dioxide evolved was first proposed by Lefèvre and Tollens[4] and later modified by Dore, McKinnis, Nanji, Paton and Ling, and Dickson, Otterson and Link.[5]

This method depends on heating the material with an excess of boiling 12% hydrochloric acid until there is no further evolution of carbon dioxide, this dioxide being absorbed in a suitable apparatus for determination.

When this method is applied to soils containing carbonates the inorganic carbon dioxide must first be determined by treatment with weak acid in such a way that decarboxylation of the uronic acid is not brought about.

The method used in the work reported here is, briefly, as follows. A three-necked 500-cc. flask was used for the reaction. Into one side neck a stream of carbon dioxide-free air was passed. Into the center neck an upright reflux condenser was fitted, the other side neck being used for the introduction of acid through a dropping funnel. The outlet at the top of the condenser was connected with a carbon dioxide absorber which consisted of a Folin–Denis bell fitted into a wide-necked Erlenmeyer flask through a two-holed stopper. The outlet from this was connected to another Erlenmeyer flask similarly equipped with a Folin–Denis bell. The outlet of this was connected to a source of suction. The incoming air was freed of carbon dioxide by passing through a soda lime tower, next through a Milliken wash bottle charged with a concentrated solution of potassium hydroxide, then through a small wash bottle detector charged with barium hydroxide solution.

The absorbers were charged with a half-saturated solution of barium hydroxide.

Twenty-five grams of soil was used, except that in the case of peat 10 g. was taken. These were placed in the flask, 200 cc. of water and enough hydrochloric acid to make a 1% solution added, and the flask heated to boiling for one hour, the carbon dioxide evolved being absorbed in barium hydroxide solution and determined as described later.

The carbon dioxide given off by this treatment for one hour was, as the work was

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[3] Schreiner and Shorey, Bureau of Soils Bulletin No. 74 (1910).

[4] Lefèvre and Tollens, *Ber.*, 25,2569 (1892); *ibid.*, 40,4153 (1907).

[5] Dore, THIS JOURNAL, 48, 232 (1926); McKinnis, *ibid.*, 50, 1911 (1928); Nanji, Paton and Ling, *J. Soc. Chem. Ind.*, 44, 2537 (1925); Dickson, Otterson and Link. THIS JOURNAL, 52, 775 (1930).

originally planned, assumed to be derived from carbonates (inorganic carbon). The absorbers were then changed or recharged, enough hydrochloric acid added to the reaction flask to make a 12% solution, the flask placed in an oil-bath and the bath heated so that the contents were kept boiling. This usually required a bath temperature of **140–145°**.

This was continued for five hours, the carbon dioxide being absorbed in barium hydroxide.

In no case was there any precipitate formed in the second absorber, even with a very rapid current of air passing through the apparatus.

At the conclusion of the operation the absorber was disconnected and the precipitated barium carbonate filtered off rapidly by suction on a small Buchner funnel. The bell and flask were rapidly washed into the funnel and the washing continued until all barium hydroxide was removed. Barium carbonate adhering to the bell and flask was then dissolved with dilute hydrochloric acid and after changing the receiver this solution was poured on the funnel, more acid being used if necessary to dissolve all the barium carbonate and the filter thoroughly washed. To the solution of barium chloride thus obtained dilute sulfuric acid was added to precipitate the barium as sulfate. This was determined in the usual way and calculated to the equivalent of carbon dioxide.

This method has a disadvantage in the danger of carbonation of the barium hydroxide solution in the process of handling and filtering, but a little experience will enable one to overcome this. It has been found that when this operation was carried out carefully and expeditiously, the maximum error was 0.5 mg. of carbon dioxide, which, when working with *23 g.* of soil, is negligible. The method has an advantage in that errors introduced by the carrying over of hydrochloric acid or other volatile products are eliminated.

The results of the examination of eleven soils are reported in this paper. The soils were as follows.

No. 1, Houston clay No. 1. No. 2, Houston clay No. 2. No. 3, Houston clay No. 3. These three were soils from experimental fields near Austin, Texas, Nos. 2 and 3 are calcareous, that is, contain enough calcium carbonate to effervesce on the addition of acid. No. 4, Chester loam from Virginia. No. 5, Norfolk fine sandy loam from North Carolina. No. 6, Washburn loam from Aroostook County, Maine. No. 7, Caribou loam from the same location. No. 8, Greenville sandy loam from DeWitt, Georgia. No. 9, Portsmouth fine sandy loam from New Bern, North Carolina. No. 10, Muck from near North Liberty, Indiana. No. 11, Everglades peat from Belle Glade, Florida. In the tables following these soils will be referred to briefly by name.

The general organic characteristics of the soils examined, together with their reaction, are stated in Table I. All determinations were made on air-dried samples and the results calculated to the oven-dried basis.

With the exception of the Houston soils, the soils have a neutral or acid reaction but appreciable quantities of carbon dioxide were given off by the treatment for one hour with 1% hydrochloric acid.

Whether this carbon dioxide is derived from inorganic carbonate, oc-

TABLE I

ORGANIC CARBON, NITROGEN REACTION

Soil	PH	Organic C	Total N	Soil	PH	Organic C	Total N
Houston No. 1	7.6	1.43	0.08	**Caribou**	4.8	3.00	0.24
Houston No. 2	8.3	0.95	.06	**Greenville**	5.4	0.96	.04
Houston No. 3	7.8	1.47	.16	**Portsmouth**	6.6	.88	.08
Chester	5.8	1.50	.17	**Muck**	6.8	30.9	3.35
Norfolk	4.7	0.82	.05	**Peat**	7.0	53.3	3.19
Washburn	5.0	4.90	.35				

cluded carbon dioxide or from the first stages of the decarboxylation of uronic acids, is under investigation.

In Table II are given the quantities of uronic acid carbon dioxide obtained after the preliminary treatment for one hour with 1% hydrochloric acid, together with the calculated equivalent of uronic acid, both being stated as percentage of the soil.

Since uronic acids are frequently a part of the more complex polyuronides, the total quantity of organic matter represented by the uronic acid carbon dioxide may be much larger than the calculated uronic acid shown in this table.

TABLE II

URONIC ACID CARBON DIOXIDE AND THE CALCULATED EQUIVALENT OF URONIC ACID PERCENTAGE OF SOIL

Soil	Uronic acid CO_2	Uronic acid	Soil	Uronic acid CO_2	Uronic acid
Houston No. 1	0.14	0.617	**Caribou**	0.36	1.587
Houston No. 2	.11	.484	**Greenville**	0.08	.353
Houston No. 3	.13	.512	**Portsmouth**	.07	.308
Chester	.24	1.058	**Muck**	1.80	7.938
Norfolk	.08	0.352	**Peat**	1.69	7.462
Washburn	.41	1.808			

Uronic acid ($C_6H_{10}O_7$) contains **37%** carbon and some idea of the proportion of uronic acid to the total organic matter of the soil may be had by comparing the uronic acid carbon with the total organic carbon. Such a comparison is made in Table III.

The theory of the evolution of furfural to the process of decarboxylation of uronic acids has already been pointed out. Carbon dioxide is first split off, leaving a pentose sugar which further breaks down to furfural and water. In other words, the decarboxylation must be complete or the formation of furfural will not be complete.

It has been contended that complete decarboxylation of uronic acids can be brought about only by heating with 12% hydrochloric acid to 135–**140**" for four or preferably five hours,[6] and with this in mind the determinations of uronic acid carbon dioxide in soils reported here were made by heating at that temperature for five hours.

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[6] **Dickson** Otterson **and Link,** THIS JOURNAL, 52,775 (1930).

TABLE III

COMPARISON OF URONIC ACID CARBON WITH TOTAL ORGANIC CARBON IN SOIL

Soil	Organic carbon in soil	Uronic acid carbon	Uronic acid carbon, percentage of total organic carbon
Houston No. 1	1.43	0.228	15.9
Houston No. 2	0.95	.179	18.8
Houston No. 3	1.47	.216	14.7
Chester	1.50	.427	28.4
Norfolk	0.82	.130	15.8
Washburn	4.90	.667	13.7
Caribou	3.00	.586	18.8
Greenville	0.96	.130	13.5
Portsmouth	.88	.113	12.8
Muck	30.9	2.86	9.25
Peat	53.3	2.75	5.15

Determinations of furfural in soils made in this Laboratory heretofore were made according to the method of the Association of Official Agricultural Chemists adopted for pentosans in feeding stuffs, and in order to have figures comparable with those previously obtained, this method was applied to the soils under discussion.

This method, which is essentially that of Kröber,[7] calls for heating to boiling with 12% hydrochloric acid at a rate such that 30 cc. distils over in ten minutes and this continued until 360 cc. has collected, which entails heating for only a little more than two hours.

It seemed that this method might give less than the theoretical quantity of furfural due to incomplete decarboxylation of the uronic acid. As a matter of fact, the quantities obtained by this method and presented in Table IV are much less than the theory calls for, and except for the peat are less than 50% of the theoretical.

TABLE IV

FURFURAL OBTAINED FROM SOILS COMPARED WITH THE CALCULATED QUANTITY

Soil	Furfural, percentage of soil	Furfural equivalent to umnic acid content	Furfural, % of calcd.
Houston No. 1	0 050	0 299	16.7
Houston No. 2	.030	.234	12.8
Houston No. 3	.037	.277	13.7
Chester	.113	.512	22.0
Norfolk	.046	.181	25.4
Washburn	.272	.881	30.8
Caribou	.141	.757	18.6
Greenville	.020	.160	12.5
Portsmouth	.050	.143	35.0
Muck	1.880	3.840	49.0
Peat	2.070	3.600	57.5

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[7] Krober, J. *Landw.*, 48, 379 (1900).

To determine whether or not this was due to the shortness of time of heating, the determinations were repeated, heating for five hours, but in no case was more furfural obtained, and in most cases slightly less.

It has been generally observed that even when working with pure uronic acids the quantity of furfural obtained is less than the theoretical, whereas the theoretical quantity of carbon dioxide is obtained. This is no doubt due to the reactivity of furfural and its tendency to form reversion products or furan derivatives. It is quite likely that in a complex mixture of organic and inorganic material, such as a soil, this tendency is accentuated with the consequent greater loss of furfural.

That this is so is indicated by the following experiment.

	Phloroglucide
0.5 g. of pectin gave	0.1284 g.
10 g. of Portsmouth sandy loam	.0140 g.
Total when determined separately	.1424
When mixed and furfural determination made the mixture gave	.1402
0.25 g. of pectin gave	.0642
10 g. of Washburn loam gave	.0490
Total determined separately	.1137
When mixed and furfural determined the mixture gave	.1020

The pectin used was the commercial "lemon pectin."

The simultaneous evolution of carbon dioxide and formation of furfural on heating with strong acid being characteristic of uronic acids and the polyuronides present in plant tissues, it seems fair to assume when soils behave in the same way that they contain uronic acids or complex substances of which such acids are a part.

The identity of such compounds is part of an investigation not yet completed, but the following data are submitted in substantiation of the foregoing conclusion.

A hot water extract of one of the soils (Houston No 3) on evaporation to dryness yielded a gray powder that amounted to 0.07% of the soil and contained 61% organic matter. Another portion of the same soil heated with water in an autoclave at 30 pounds pressure yielded a similar extract, 0.11% of the soil and containing 76% organic matter.

Both these extracts were readily soluble in water again with the exception of a small portion (about 5%) that was inorganic in nature. Such a water solution gave the following reactions. It gave a strong Molisch reaction. It did not reduce Fehling's solution but did so after heating for a few minutes with hydrochloric acid. This reducing property, however, soon disappeared on continued heating with acid. Heated with hydrochloric acid and a small portion of orcin a green color was formed. Heated with hydrochloric acid and naphthoresorcinol, it gave a dark colored precipitate which was soluble in ether with a reddish-violet color, and in warm benzene with a blue color. These color reactions, with the exception of that with naphthoresorcinol, are given by pentoses or pentose yielding material.

When the water solution is subjected to dialysis there is left a somewhat opalescent viscous solution or dispersion from which several volumes (four or five) of 95% alcohol throw down a gelatinous precipitate which readily can be filtered off. This, when treated with water, forms again an opalescent dispersion which gives all the color reactions mentioned much more strongly than the original solution of the extract.

The residue from hot water extraction on heating with 12% hydrochloric acid gave 2.5% of furfural.

The residue from the water extract made under pressure when heated with 1% hydrochloric acid for one hour gave 0.5% of carbon dioxide and heating further for five hours with 12% hydrochloric acid gave 3.24% of carbon dioxide.

It is evident that water extraction under pressure as in this case extracts but a small portion of the uronic acid constituents. This soil (Houston No. 3) contained uronic acid carbon dioxide 0.13%, whereas calculating the 3.24% of the water extract back to the original soil gives but 0.0035% of uronic acid carbon dioxide.

A further separation of uronic acid material from soil was effected in the following manner. The soil was treated with 2% sodium hydroxide until the extract gave a strong Molisch reaction—this sometimes required several days. The supernatant liquor was decanted from the soil, made slightly acid with acetic acid, excess of barium carbonate added and the liquor concentrated to about one-quarter of its volume, filtered and further concentrated until it became sirupy.

This sirup, when poured into four volumes of 95% alcohol, formed a gelatinous precipitate which was readily filtered off and washed with alcohol. This precipitate dries to a horny mass which, when pulverized, forms a light gray powder. The precipitate or the dry powder when treated with water forms an opalescent solution or dispersion—more readily if a small quantity of barium acetate be added. This solution gives a precipitate of barium sulfate on addition of sulfuric acid and is evidently a barium salt or contains a barium salt of some uronic acid complex. The solution obtained in this way gave all the color reactions noted in connection with the water extract. The dry powder when heated with 12% hydrochloric acid gave off both carbon dioxide and furfural.

Separations of this kind were made from two of the soils (Houston No. 3 and Chester loam) and no differences have been noted in the character of the material so obtained. A larger quantity could be obtained from the Chester loam than from the Houston soil and larger quantities are obtainable by extraction with alkali than by water extraction.

The demonstration of the presence of uronic acid or polyuronides in soils is, in itself, the establishment of a new fact in regard to the character of the organic matter of soils, and further interest immediately connected with this fact lies in the identity of these uronic acid compounds, their origin and fate in the soil. These, naturally, are under investigation.

There are at least two points of a more or less analytical nature raised by the work here reported. One is the determination of inorganic carbon (carbonates) in soils. It is quite evident that heating soil with 1% hydrochloric acid gives rise to an evolution of carbon dioxide that, in some cases, one can scarcely conceive of as being present as inorganic carbonates. For instance, of the soils discussed in this paper five have a strong acid reaction and on heating for one hour with 1% hydrochloric acid, gave the following quantities of carbon dioxide.

These quantities of carbon dioxide were not included in stating the quantity of uronic acid carbon dioxide in Table II, but it is likely that they arise from the initial decarboxylation of uronic acids and should be added

TABLE V

CARBON DIOXIDE OBTAINED BY HEATING FOR ONE HOUR WITH 1% HYDROCHLORIC ACID

Soil	PH	Carbon dioxide, per cent. of soil
Chester	5.8	0.124
Norfolk	4.7	.044
Washburn	5.0	.204
Caribou	4.8	.220
Greenville	5.4	.075

to the figures stated there, but in view of the uncertainty as to their origin they were ignored. It seems quite probable that many of the discrepancies observed in determinations of carbon dioxide in soils have been due to variations in temperature and strength of acid used.

The other point is in connection with what may be called proximate analysis of soil organic matter. The most recent and probably at present the best known of such methods is that proposed by Waksman and Stevens.[8]

By this method the organic matter is separated into fractions: ether soluble, water soluble, alcohol soluble, hemicelluloses, cellulose, lignin, etc.

Apart from certain fundamental concepts that lead to erroneous conclusions in the application of this method, the most serious defect lies in that no place is provided for classes of organic soil constituents that from time to time may emerge from the obscurity of humus investigations. Uronic acids or polyuronides furnish an example of this. These are not soluble in ether or alcohol and are only very slightly extracted by hot water. On heating with acid, as the method calls for in the determination of hemicelluloses, they disappear as carbon dioxide and furfural, and such reducing sugar as might be formed from polyuronides completely disappears under the treatment.

Link and Niemann[9] have recently contributed to our knowledge on this point, showing that when polyuronides are hydrolyzed with weak acids the uronic acids split off and are destroyed as soon as formed.

We find, then, that a class of organic compounds that occur in soils that may represent from 5 to 25% or more of the organic carbon is, by this method, not only ignored, but so far as determination is concerned, is almost completely eliminated.

Summary

In this paper there are presented results of the examination of eleven samples of soil for the presence of uronic acid, according to methods adopted and in use for the determination of these acids in vegetable products.

The soils are from eight locations and represent types varying from sandy loams containing 0.82, 0.88 and 0.96% of organic carbon, to loams contain-

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[8] Waksman and Stevens, *Soil Science*, **26**, 113 (1928).

[9] Link and Niemann, THIS JOURNAL, **52**, 2474 (1930).

ing 3.00 and 4.90% of organic carbon, a muck containing **30%** and a peat containing 53% organic carbon. These soils varied in reaction from PH 4.7 to 8.3.

The uronic acid carbon dioxide varied from **0.07** to **1.80%** of the soil, and this, when calculated to the equivalent uronic acid, varied from 0.308 to 7.94% of the soil.

The uronic acid carbon calculated from these figures varied from **0.113** to 2.86% of the soil and this uronic acid carbon varied from 5.15 to 28.4% of the total organic carbon.

The presence of uronic acids or complex substances containing them (polyuronides) was confirmed by the separation from two of the soils of colloidal material having all the properties of such uronic acid complexes.

This separation was made both by hot water extraction and extraction with dilute sodium hydroxide.

The bearing of the presence of uronic acids in soils on certain analytical operations has been pointed out. These are the determination of carbonates in soils, and methods proposed for the proximate analysis of the organic matter of soils.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

THE POTENTIALS OF SOME UNSTABLE OXIDATION–REDUCTION SYSTEMS

BY LOUIS F. FIESER

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Although a considerable amount of data concerning the oxidation–reduction potentials of well-defined organic systems has accumulated during the past ten years, relatively few efforts have been made to study by direct potentiometric measurement those systems which are alterable and with which the potential of a solution is subject to a definite drift with time as the result of some reaction which consumes either the oxidant or the reductant, or both. Such systems, to be sure, have been studied by colorimetric and electrometric indicator methods, but these are to be classed as indirect methods inasmuch as they involve the observation of the effect of the unstable system upon the color or the potential of an oxidation–reduction system of unalterable components, and it is the potential of the latter, rather than that of the former, which actually is measured.

The potential of the alterable system has been the basis of observation in only a few investigations. Biilmann and Blom[1] have recorded the equilibrium potentials, together with the velocity constants, for the disappearance of the reductant, for two azo–hydrazo systems. They followed the

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[1] Biilmann and Blom, J. *Chem. Soc.*, **125**, 1719 (1924).

fairly slow drift in the potentials of solutions prepared from equimolecular amounts of the oxidant and reductant and extrapolated the values to zero time. Relying not upon extrapolation but upon initial potentials obtained as soon as potentiometric balance could be reached, Clark, Cohen and Gibbs[2] obtained data for the systems from benzidine, o-tolidine and *p*-aminodimethylaniline, but their "attempts to measure the system of which p-phenylenediamine is the reductant were frustrated by the extreme instability of the system." In addition to these studies, Conant and Fieser[3] have reported approximate results obtained by rapid titration for the *o*-benzoquinone–catechol system, while Conant and Pratt[4] give some record of their attempts to measure the potential of the system formed by *p*-aminophenol and its highly alterable oxidation product, quinone-imine, and state that even under the most favorable conditions "the value of the oxidation-. reduction potential cannot-be determined accurately."

It is an unfortunate circumstance that the instability of the simple quinone-imines, quinonedi-imines and certain of the quinones has imposed such limitations upon the investigator as to prevent the accurate evaluation of the free energy of reduction of these substances, for some of the most interesting compounds fall into this group. On the more practical side, it will be recalled that the substances in question, in the form of their reduction products, have been used extensively as oxidation–reduction indicators and as photographic developers. Their suitability for these purposes is determined largely by the potentials of the systems.[5]

There is thus abundant reason for attempting to extend to some extent the limits in the field of the direct measurement of the oxidation–reduction potentials of unstable systems. We have examined several such systems with which, while the reductant is perfectly stable, the oxidant undergoes decomposition with greater or less rapidity when it is prepared in aqueous solution or in a mixture of water and alcohol. It did not appear expedient to prepare the oxidant in non-aqueous medium even where this is known to be possible, for a certain unnecessary period of time would be required for the dissolution of the material in the electrolytic solvent. It seemed much more rational to start with a solution of the reductant and to produce the oxidant in the solution at the time desired by the addition of an oxidizing agent. Ordinary electrometric titration of the reductant, however, is out of the question when a highly alterable oxidant is concerned. The decrease in potential between successive increments of the oxidizing agent is often so rapid that the results are meaningless.

The method which we have adopted as being the most satisfactory of any

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[2] Clark, Cohen and Gibbs, Pub. *Health Repts.*, Supplement No. 54, 1926

[3] Conant and Fieser, THIS JOURNAL, 46, 1858 (1924).

[4] Conant and Pratt, *ibid.*, 48, 3179 (1926).

[5] Compare Frary and Nietz, *ibid.*, 37, 2246 (1915).

yet developed may be called that of discontinuous titration. To a solution of the reductant there is added an amount of oxidizing agent estimated to produce a certain amount of the oxidant and thus to fix, at least momentarily, the ratio of oxidant to reductant. The potential of the solution is observed and followed with time. In further experiments the same quantity of reductant is treated with varying amounts of oxidizing agent so that, when all of the experiments are grouped together, a composite titration curve may be constructed and from it the normal oxidation–reduction potential and other constants may be calculated. This general scheme was employed to a certain extent by Clark, Cohen and Gibbs in the work cited, and its advantages over the continuous titration method are apparent. The most important point of difference in the present work lies in the manner of interpreting the potential readings. The choice lay between extrapolating the time–potential curve, after the manner of Biilmann, or in taking the first measurable potential, according to Clark, but the experiments themselves soon furnished reasons for giving preference to the former method. This will be shown directly, in connection with a description of some of the results obtained.

The Method of Procedure

In performing each experiment a solution of 0.0003 mole of the reductant was employed. In the case of the amines it was found convenient to prepare a 0.015 M solution of the amine hydrochloride and to add 20 cc. of this to 190 cc. of the buffer solution. Well-poised buffer solutions having a high concentration of salts (usually 0.2 *M*) were chosen in order to prevent any but very slight changes in hydrogen-ion concentration as a result of the dilution or the presence of the sample. When 0.1 M hydrochloric acid was the solvent, the PH employed was that found for the diluted solution. As the electrode vessel a tall 400-cc. beaker was employed, and the solution of the reductant was agitated vigorously in the thermostat with an efficient mechanical stirrer. The oxidizing agent used was a 0.03 M aqueous solution of potassium molybdicyanide, $K_3Mo(CN)_8$.[6] Since an unnecessary amount of time is consumed in running in the reagent from a buret, the addition was made in the following way. The reagent was carefully measured into a small dropping funnel having a wide-bore stopcock, and the stem of the funnel was inserted through the stopper of the electrode vessel. A rapid-delivering Mohr buret containing buffer solution was clamped just above the dropping funnel so that the latter could be rinsed out quickly into the vessel. When all was in readiness the stopcock was turned and the stop watch was released just as the stream of the oxidizing solution entered the stirred solution. With this arrangement it was possible to introduce 3–20 cc. of molybdicyanide solution in not more than three seconds, with about one second more for the rinsing. The potential readings were made on a student's type potentiometer and with an enclosed glass and scale galvanometer. By placing the stop watch in line of vision with the galvanometer scale and having this directly behind the potentiometer dial, the unassisted observer had little difficulty in following a very rapidly changing potential. Readings were made at intervals of fifteen seconds.

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[6] Some observations concerning the preparation and stability of this reagent will be published in another paper.

The average volume of the solution at the time of the measurement was *220* cc. and the total concentration of the organic system *0.0014* M. When it was desirable to keep the volume the same in all experiments the amount of buffer solution used for washing out the funnel was so adjusted as to make the final volume just *230* cc.; total concentration, *0.0013 M.* The temperature was *25°* in all of the experiments.

***p*-Benzylaminophenol[7]-N-Benzyl-quinone-imine.**—The potential of a solution of these components in every case decreased rapidly with time, but the rate of change usually varied with the nature of the solvent and with the ratio of oxidant to reductant. The simplest behavior noted is illustrated by Curve II of Fig. 1. It will be observed that for one and one-fourth minutes the relationship between the decrease in potential and the time is linear.

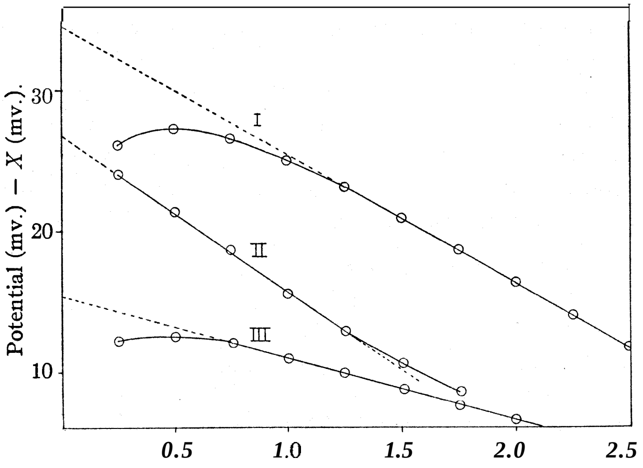

Fig. 1.—The system: *p*-benzylaminophenol–N-benzyl-quinone-imine. Curve I, P_H *7.57*, [Oxid]/[Red] = *6.25;* Curve II, P_H *1.10,* [Oxid]/[Red] = *0.387;* Curve III, P_H *7.57,* [Oxid]/[Red] = *0.403.*

The fact that the potential decreases indicates that it is the oxidant which is being destroyed, and the nature of the relationship points to a first order reaction, for both the monomolecular velocity constant and the potential of the solution are logarithmic functions of the concentration of the oxidant. The velocity constant may be defined by the following equations

$$k' = \frac{2.3026}{t} \log \frac{[\text{Oxid}]_i}{[\text{Oxid}]_i - x} \qquad (1)$$

$$E_i - E_t = \frac{RT}{nF} \log \frac{[\text{Oxid}]_i}{[\text{Oxid}]_i - x} \qquad (2)$$

$$\text{Let } k = kRT/2.3026\,nF$$

$$k = (E_i - E_t)/t \qquad (3)$$

The initial concentration of the oxidant is denoted by $[\text{Oxid}]_i$, x is the amount which has disappeared in *t* minutes, E_t is the potential at that time

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[7] The material was crystallized as the hydrochloride.

and E_i is the initial potential of the solution. If the initial potential is taken as that found on extrapolating Curve II to zero time, the following values are obtained for the velocity constant, k (Table I). Up to one and one-fourth minutes the constancy is very good; the velocity then progressively decreases. Though the period over which the monomolecular reaction rate holds good is very brief, it may be estimated from other data on hand that the potential is a linear function of the time up to the point where 52% of the oxidant originally present has disappeared. The constancy is thus maintained for a considerable part of the life of the oxidant. It is clear that the reaction is monomolecular in the early stages, and one is consequently justified in making the extrapolation indicated by the dotted line. The only uncertainty is concerned with the timing of the experiment, but every effort was made to reduce this uncertainty to a minimum. The possible error in fixing the zero time is about two seconds, which in the case at hand would amount to an error of **0.0005** v. in the value for the initial potential.

TABLE I

VELOCITY CONSTANTS FOR REACTION PLOTTED IN CURVE II, FIG. 1

Minutes	Potential	k	Minutes	Potential	k
0	0.6880 (Extrap.)	....	1.50	0.6717	(0.0108)
0.25	,6852	0.0112	1.75	.6697	(.0104)
.50	.6825	.0110	2.00	.6677	(.0101)
.75	.6798	.0109	2.25	.6654	(.0100)
1.00	.6767	.0113	2.50	.6637	(.0097)
1.25	.6740	.0112	2.75	.6624	(.0093)

One significant conclusion to be drawn from the results just quoted is that in fifteen seconds the mixing is complete, the reaction between the reductant and the molybdicyanide has gone to completion, and electrode equilibrium has been attained. The potential at this point could hardly show the concordance with the succeeding potentials if it were otherwise. While the same observations apply equally well to many other experiments, there were other cases in which the first potential readings (15 sec.) did not fall into line with the rest in this manner, and examples of this type of behavior are given in Curves I and III of Fig. 1. Like Curve II, these results refer to the system from p-benzylaminophenol, but in neutral rather than acid solution. Instead of falling off at once, the potential shows a slight increase after fifteen seconds and only begins to drop in direct proportion to the time after one and one-fourth minutes for Curve I, and forty-five seconds for Curve III. In view of the conclusions drawn from the form of Curve II, this lag can hardly be due to incomplete mixing and it probably is not occasioned by a tardy establishment of electrode equilibrium. We are thus led to believe that the reaction between the reductant and the molybdicyanide is complete only after the time intervals noted. After the period of lag the reaction follows the monomolecular course for seven minutes, and we have extrapolated the straight portions of the curve (dotted lines) in order to obtain the initial potentials.

The initial potential obtained in this way is subject to some error if our interpretation of the lag is correct, for the amount of oxidant initially available for the decomposition reaction is not quite as great as that which the extrapolation curve implies. It seems unlikely that the phenomenon is the result of a slow attainment of potential balance, but if this is actually the case no error would be involved other than that occasioned by the extent of the extrapolation necessary. While we see no way of either obviating or evaluating this possible source of error, there is reason to believe that the error is very slight. Curves I and III both refer to the discontinuous titration of p-benzylaminophenol at P_H 7.57 and the experiments differ only in that the value of the ratio [Oxid]/[Red] was 6.25 and 0.403, respectively. Now there is much more lag, and more error if any, in the first case than in the second and yet the calculations from both experiments indicate very nearly the same value for the normal oxidation–reduction potential of the system. The case at hand, moreover, was selected for illustration because it is an extreme one; many other experiments might be cited in which a lag in the time–potential curve occurred only when the concentration of the oxidant was relatively high, and in these instances there was no detectable difference in the results for the experiments which showed this lag. There is thus justification for regarding extrapolations of the type illustrated in Curves I and III as at least close approximations.

The method which we have adopted for fixing the initial potential of the solution thus consists in extrapolating the first observed straight portion of the time–potential curve to zero time. A comparison may now be made with the procedure of Clark, Cohen and Gibbs, who took for this value the reading obtained as soon as potentiometric balance could be reached. In their experiments this required about twenty seconds; in our work the first reading was made at exactly fifteen seconds, and we are reasonably sure that a true balance had been attained. According to the interpretation which we have made of Curve II, during the time required for the attainment of electrode equilibrium and for the mechanics of measurement a considerable amount of oxidant has disappeared and the potential has fallen an appreciable extent. In other words, the error of taking the first measurable potential as the initial potential here amounts to 2.5 mv. In the case of the experiment of Curve I the error would be more serious. If one were relying entirely upon the first "significant potential" one very probably would conclude that electrode equilibrium had been reached at thirty seconds and that the potential found here was the true potential. According to the results of extrapolation the error would amount to 7.3 mv. While we thus feel that the method of Clark, Cohen and Gibbs should not be used in the study of the systems with which we are here concerned, we do not wish to imply a criticism of their own work. Each system has its own peculiarities and may require a special method of study.

Having described our method of fixing the initial potential, E_i, we shall present in Table II a summary of a typical "discontinuous titration." The potentials given are single electrode potentials at 25° referred to the hydrogen electrode potential at PH 0.

TABLE II

SYSTEM: *p*-BENZYLAMINOPHENOL-N-BENZYL-QUINONE-IMINE

PH 7.57. End-point = 17.4 cc. molybdicyanide solution

Molybdicyanide soln., cc.	Initial potential, E_i, v.	$\frac{[\text{Oxid}]}{[\text{Red}]}$	0.02957 × log R, v.	C	E_n, v.	k
3.0	0.2227	0.208	−0.0201	1.35	0.2506	0.0043
5.0	.2338	.403	− .0117	1.37	.2501	.0047
7.0	.2427	.673	− .0051	1.37	.2498	.0057
9.0	.2514	1.07	.0009	..	.2502	.0066
11.0	.2595	1.72	.0070	1.38	.2498	.0072
13.0	.2695	2.95	.0139	1.42	.2502	.0082
15.0	.2831	6.23	.0235	1.42	.2504	.0092
				Av. 1.39	Av. 0.2501	

The end-point of the titration was determined in the usual way except, of course, that a number of separate experiments were required, in each of which a different amount of oxidizing agent was added to the solution of the reductant. This method was found preferable to the use of standardized solutions of the molybdicyanide and of the reductant on account of some uncertainties in these standardizations. It is not difficult to ascertain the end-point with a reasonable degree of accuracy, even with these unstable systems, and often one is aided by a distinct color change.

The initial potentials obtained by extrapolation are given in the second column of the table and they are represented graphically in Fig. 2. The full line drawn through the potentials forms a smooth curve which has the logarithmic form of the usual titration curve but not the slope. For a reductant which loses two hydrogen atoms on oxidation, the slope of the curve is normally represented by the equation

$$E = E_n + 0.02957 \log \frac{[\text{Oxid}]}{[\text{Red}]} \qquad (4)$$

in which E_n is the potential when [Oxid] = [Red] in a given solution. This equation is pictured in the figure by the dotted line. The present results may be represented by the modified Equation, 3, by the introduction of an empirical constant, C, to correct for the divergent slope

$$E = E_n + C \times 0.0295 \log [\text{Oxid}]/[\text{Red}] \qquad (5)$$

At the point of half-oxidation the two equations become identical, and the potential corresponding to this point provisionally may be taken as the value for E_n. Using this value one may now calculate from Equation 5 the value of the constant, C, as has been done in the fifth column of the table. In the fourth experiment the ratio [Oxid]/[Red] is so close to unity that a calculation of C is not admissible. The constancy is sufficiently good to show that the equation accurately expresses the results.

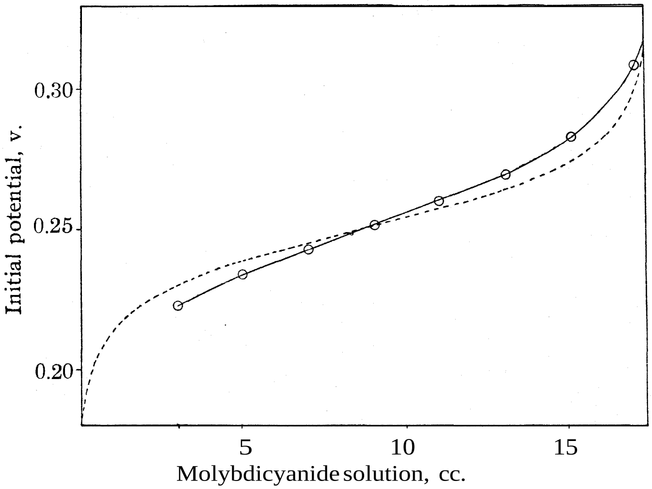

Fig. 2.—Titration curve of *p*-benzylaminophenol at PH 7.57.

An explanation of the abnormal slope is not far to seek. Several investigators have noted the influence on the potential of the quinone–hydroquinone system of the association between the components to form quinhydrone, and Clark, Cohen and Gibbs have found that such association is particularly marked among the systems of the *p*-phenylenediamine series, to which the system under study is closely related. Conant and collaborators[8] ascribed abnormal slopes of the titration curves of certain anthraquinones to quinhydrone formation. It is probable that quinhydrones or meriquinones are formed in the present case, and with most of the other substances reported on below. If the meriquinone, M, contains equal molecules of oxidant and reductant, Equation 4 must be modified as in 6

$$E = E_n + 0.02957 \log \frac{[\mathrm{Oxid}]_T - [\mathrm{M}]}{[\mathrm{Oxid}]_T - [\mathrm{M}]} \qquad (6)$$

The terms $[\mathrm{Oxid}]_T$ and $[\mathrm{Red}]_T$ refer to the total amounts of the components. It is evident that the removal of equivalent amounts of oxidant and reductant from the oxidation–reduction equilibrium would shift the potential to values progressively higher than the normal as the excess of oxidant over reductant increases, and to lower values as this ratio is reversed.

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[8] Conant, Kahn, Fieser and Kurtz, THIS JOURNAL, 44, 1382 (1922).

The magnitude of the effect in the present instance may be estimated by relating Equations 5 and 6, and for this purpose we shall make use of an expression similar to that developed by Conant.[8,9] If the oxidant is present in excess of the reductant, and if X is the degree of association of the complex, M, then $[M] = X[\text{Red}]_T$. Expressing the concentrations of oxidant and reductant in terms of the ratio, R, of the former to the latter, the following expression is obtained.

$$E = E_n + 0.02957 \log \frac{R - X}{1 - X} \tag{7}$$

When it is the reductant which is in excess, the equation is

$$E = E_n + 0.02957 \log \frac{R - RX}{1 - RX} \tag{8}$$

To obtain the degree of association, X, Equation 7 may be combined with the empirical Equation 5, whence

$$C \log R = \log \frac{R - X}{1 - X} \tag{9}$$

Using the average value found for the constant, C, one finds the value of 0.36 for X when R = 2; 0.52 when R = 5. This indicates that the meriquinone formation takes place to a considerable extent.

Some caution should be exercised in respect to conclusions deduced in this way concerning meriquinone formation, for the subject is full of complications, as Clark, Cohen and Gibbs have pointed out. We have presented a possible interpretation of the peculiar titration curves, but in reporting our results we prefer to disregard the theoretical aspects of the question and to make use of the empirical Equation 5. A provisional value for E_n, the potential at half-oxidation, was obtained by interpolating the titration curve, and from it an average value for the constant, C, was calculated. We may now reverse the process, that is, use the average value found for C and calculate E_n from the results of each experiment. This has been done in the sixth column of Table II. The agreement between the individual values is very good, considering the rapid decomposition of the oxidant, the abnormal slope of the titration curve, and the lag in the time–potential curve (Curves III and I of Fig. 1 refer to the second and the last experiments of Table II).

Values for the velocity constant of the decomposition reaction are given in the last column. Since, by definition, $k = (E_i - E_t)/t$, the values for k represent the drop in potential per minute. In each case the rate remained constant for from six to seven minutes and the values reported represent the averages during the period of constancy. It will be observed that the velocity increases very considerably as the concentration of the oxidant is increased, though the changes are not parallel. A five-fold

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[9] Conant's equation, p. 1391, holds when the reductant is in excess but not for the converse case.

increase in the concentration of the oxidant doubles the velocity constant. It is thus difficult to classify the order of the reaction as a whole, though in each individual experiment it appears to be strictly monomolecular in the early stages.

The oxidation of *p*-benzylaminophenol was not followed in the alkaline range, but a fairly complete study was made in acid and neutral solutions. A condensed summary of the results is given in Table III. The individual experiments at each PH are not recorded, but an indication of the agreement of the six or seven determinations of each value for E_n is given by appending the average error. Single electrode potentials on the hydrogen scale at 25° are given. Except in the first case, the solutions all contained a total of 0.2 M per liter of buffer salts. Some indication of the velocity constants observed is given by including in the last two columns the approximate constants for two values of the ratio [Oxid]/[Red], R. Experiments were not usually performed at just the ratios indicated, but the constants were obtained by interpolation.

TABLE III

VARIATION OF THE POTENTIAL OF THE SYSTEM *p*-BENZYLAMINOPHENOL–N-BENZYLQUINONE-IMINE WITH HYDROGEN-ION CONCENTRATION

PH[10]	Hydrogen electrode potential, E_n, v	Constant, C, of Eq. 5	Potential when [Oxid] = [Red], E_n, v	Av error, mv	Calcd. E, v.	Diff. E_n (Found–calcd.), mv	Velocity constant, k when [Oxid]/[Red] = 0.3	3.3
1.10	–0.0648	0.82	0.6992	0.4	0.6991	0.1	0.011	0.010
1.56	.0925	.84	.6715	.4	.6708	.7	.011	012
2.05	.1214	1.14	.6391	.4	.6407	–1.6	.011	.012
2.69	.1589	1.00	.5976	.2	.5957	1.9	.011	.016
3.22	.1903	1.24	.5609	.3	.5578	3.1	.014	.024
3.53	.2086	1.18	.5346	.3	.5332	1.4	.012	.021
3.88	.2296	1.19	.5048	.6	.5036	1.2	.008	013
4.32	.2558	1.23	.4651	.7	.4665	–1.4	.003	.006
4.91	.2903	1.09	.4163	.3	.4195	–3.2	.002	.003
5.58	.3301	1.32	.3707	.9	.3718	–1.1	.002	.003
6.96	.4114	1.29	.2878	1.1	.2872	0.6	.007	.011
7.57	.4475	1.39	.2501	0.2	.2509	– .8	.005	.008

$E_0 = 0.6984$ $K_0 = 9.00 \times 10^{-12}$ $K_r = 1.48 \times 10^{-9}$

The first two series of experiments summarized in the table require a more detailed description. At PH 7 the potential of the molybdicyanide–molybdocyanide system is over 0.4 v. higher than that of the organic system, hence the reaction between potassium molybdicyanide and *p*-benzylaminophenol proceeds practically to completion at all concentrations of the reactants and a sharp inflection at the end-point of a titration is ob-

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[10] The buffer solutions were of the following compositions: PH 1.10, HCl; PH 1.56–2.05, glycine, HCl, KCl; PH 2.69, citric acid, NaOH, NaCl; PH 3.22–3.88, KH-Phthalate, HCl; PH 4.32–4.91, sodium acetate, acetic acid, NaCl; PH 5.58, citric acid, NaOH, NaCl; PH 6.96–7.57, Na_2HPO_4, KH_2PO_4.

tained. But the potential of the organic system, in reference to a hydrogen electrode at the same P_H, increases somewhat with increasing acidity while that of the inorganic system suffers an enormous decrease, with the result that at P_H 1.10 the potentials of the two systems overlap and the reaction between the reductant and the oxidizing agent comes to a stop when an appreciable quantity of the molybdicyanide is still unconsumed. This does not necessitate giving up this oxidizing agent, but it does require that a correction be applied for the unreacted reagent.

The fraction, m, of the potassium molybdicyanide which has failed to react may be found from the potential of the solution and Equation 10

$$E = E\ (\mathrm{Mo}) + 0.05915 \log m/(1 - m) \tag{10}$$

where E (Mo) is the potential of a half-oxidized molybdicyanide solution at P_H 1.10 on the hydrogen scale and **E** is the initial potential of the mixture of organic and inorganic materials, on the same scale. **A** rough determination of E (Mo) suffices for the purpose at hand and the value used was 0.771 v., determined by titration with potassium ferrocyanide. If the end-point in the titration of *p*-benzylaminophenol, preferably as determined in another series of experiments at a higher P_H, be represented by **P** and if C cubic centimeters of molybdicyanide solution is employed in a given experiment, the correct ratio of oxidant to reductant (R) is given by Equation 11

$$R = \frac{C\ (1 - m)}{P - C\ (1 - m)} \tag{11}$$

Table IV gives the details of the results and calculations at P_H 1.10. The titration curve is not as steep as one would anticipate and there is a downward trend in the values for E_n obtained by applying the usual equation (next to last column). This cannot be caused by association between the oxidant and reductant for the trend is in the wrong direction. Indeed we have failed to discover the cause for this, but we have corrected for it by means of the empirical Equation 5, and there is reason to accept the values thus obtained for E_n (last column), for the average is identical with the mid-point potential of the titration curve.

TABLE IV

TITRATION OF *p*-BENZYLAMINOPHENOL AT P_H 1.10

End-point (P) = 17.2 cc.

Molybdicyanide soln. added, cc.	Initial potential, E_i, v.	Fraction of Mo soln. unreacted, m	$\frac{[\mathrm{Oxid}]}{[\mathrm{Red}]} = R$	Constant, C, of eq. 5	Potential when [Oxid] = [Red]. E_n (uncorr.), v.	Potential when [Oxid] = [Red]. E_n (corr.), v.
5.0	0.6881	0.038	0.387	0.90	0.7002	0.6991
7.0	.6949	.049	.630	.74	.7008	.6997
9.0	.6994	.057	.977	..	.6997	.6997
11.0	.7037	.067	1.49	.88	.6986	.6995
13.0	.7081	.078	2.30	.83	.6974	.6993
15.0	.7121	.091	3.77	.77	.6951	.6982

In the experiments at PH 1.56 there was some overlapping in the potentials of the organic and inorganic systems, except for very low values of R, and the correction was applied in the same way, using 0.782 v. as the value for E (Mo).

No general conclusions can be drawn regarding the velocity of decomposition of the oxidant, as inspection of the values for k in Table III will show. There is no definite trend with changing acidity; the rate is sometimes constant over a considerable range of concentration of the oxidant, but it often increases decidedly as the amount of the quinone-imine increases.

Some statement should be made regarding the color of the solutions at the conclusion of the experiments. From *P*H 1.10 to 3.53 the solutions were yellow; at *P*H 3.88 a faint purple developed, and at PH 4.91 and beyond a red precipitate resulted from the oxidations. In the case of the highly colored solutions or suspensions a striking and significant effect was noted. **As** the end-point of the titration was approached the solution became pale purple, and when this point had been reached or passed the solution was pure yellow in color. The more intense color is thus caused either by an association or an interaction of the quinone-imine or its decomposition products with the reductant.

We shall now turn to the interesting problem of determining whether the potentials of this system have been characterized accurately enough to reveal the dissociation constants of the oxidant and reductant. In Fig. **3** the potentials of half-oxidation of Table III are plotted against the PH of the buffer solutions. It will be observed that the points fall on a smooth curve which has certain distinct characteristics. Starting in the neutral range, there is a straight portion which is parallel to the curve for the hydrogen electrode potential and thus has the slope 0.05915 log $[H^+]$. This "0.06 slope" is characteristic, though not uniquely so, of a system in which an oxidant or reductant is either un-ionized or completely ionized, and in the present case it is altogether reasonable to assume that they are un-ionized. Close to PH 5 there is an upward inflection and the curve then approaches an "0.09 slope." This indicates that a dissociation of some basic group begins to occur at about this acidity. That the potential becomes higher than when the components of the system are un-ionized means that it is the reductant which dissociates, for the removal of some of the undissociated reductant from the oxidation–reduction equilibrium by ionization would increase the ratio

[Undissociated Oxidant]/[Undissociated Reductant]

and hence shift the potential to higher levels. The dissociation of the reductant is complete when the "0.09 slope" is reached, but a second inflection in the opposite direction is noted at PH 2.85 and the curve then swings back to a new "0.06 slope." This obviously indicates a basic ionization of the oxidant, which eventually compensates for the dissociation of the reductant and brings the curve once more parallel to that for the hydrogen electrode.

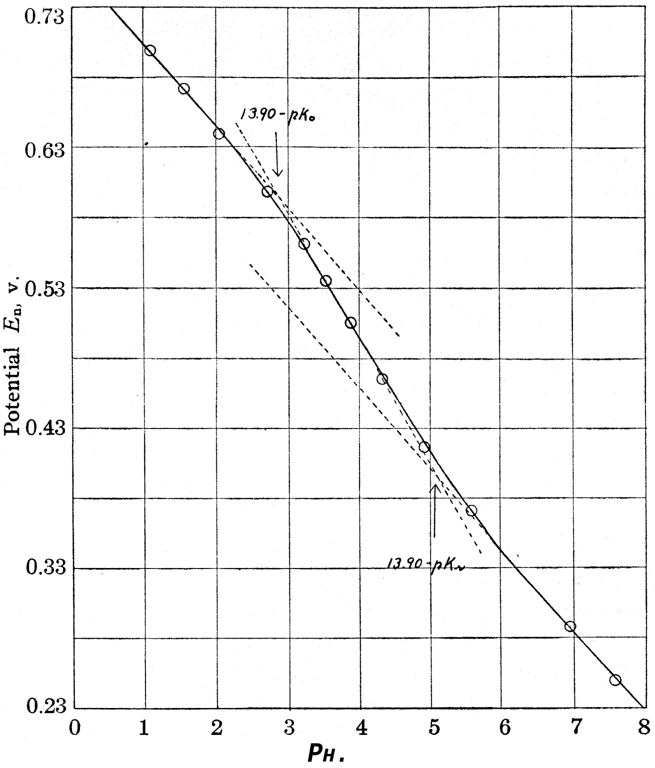


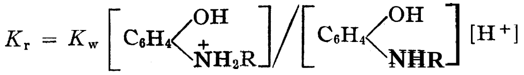
Fig. 3.—Relationship between PH and the potential of half-oxidation of *p*-benzylaminophenol. (The line is theoretical, the points experimental.)

Since the study of the system has not been pursued into the alkaline range, we may omit all consideration of the acidic ionization of the reductant in developing an equation to cover the present observations. For the limited PH region investigated the equation for a system in which the oxidant and the reductant have the basic dissociation constants, K_o and K_r is as follows

$$E_n = E_0 + E_h + 0.02957 \log \frac{K_w + K_r [H^+]}{K_w + K_o [H^+]} \qquad (12)$$

The term E_n is the potential when [Oxid] = [Red], E_0 is the normal oxidation–reduction potential for the undissociated components of the system, E_h is the hydrogen electrode potential, K_w is the ionization constant of water, for which we have used the value 1.26 × 10^{-14} and K_o and K_r are defined as follows

$$K_o = K_w \left[C_6H_4 \begin{matrix} \diagup O \\ \diagdown \overset{+}{N}HR \end{matrix} \right] \Big/ \left[C_6H_4 \begin{matrix} \diagup O \\ \diagdown NR \end{matrix} \right] [H^+] \qquad (13)$$



$$K_r = K_w \left[C_6H_4 \begin{matrix} \diagup OH \\ \diagdown \overset{+}{N}H_2R \end{matrix} \right] \Big/ \left[C_6H_4 \begin{matrix} \diagup OH \\ \diagdown NHR \end{matrix} \right] [H^+] \qquad (14)$$

With the aid of this equation we have constructed a "best curve" to fit the experimental results, and the constants which we have thus found for the system are given at the bottom of Table III. In the sixth column of this table are to be found values for E_n for each PH as calculated from Equation 12 and the constants, and a comparison between the values found and those calculated is given in the following column. For further comparison the theoretical equation has been plotted in Fig. **3,** and it will be seen that the experimental values (points) lie close to the curve. Comment on these results will be reserved until other systems have been defined.

In addition to the measurements in aqueous solution, some knowledge of the nature of the system in an alcohol–water mixture was desirable. The solvent chosen contained primary and secondary phosphates in such a ratio as to give a solution of PH 7.03 in water, and we considered that very little ionization of either the oxidant or reductant would occur in the neutral solution and hence that the potential difference between the oxidation–reduction electrode at half-oxidation and the hydrogen electrode in the same solvent would give an adequate measure of the "normal" oxidation–reduction potential. The cell employed was that just indicated, and we shall term the e. m. f. of this cell the normal potential E_0 for the alcoholic solution. The results of a "discontinuous titration" are given in Table V. Comparison with the results in aqueous solution shows that the normal potential is very nearly the same (compare 0.6984), but that the velocity of the disappearance of the oxidant is noticeably less in the alcoholic buffer than in the neutral aqueous solutions.

TABLE V

POTENTIALS OF THE SYSTEM *p*-BENZYLAMINOPHENOL–N-BENZYL-QUINONE-IMINE

Solvent: 37% alcohol, 0.038 M in KH_2PO_4, 0.067 M in Na_2HPO_4

Initial potential, E_i, v.	$\frac{[\text{Oxid}]}{[\text{Red}]}$	Const., C, of Eq. 5	Normal potential, E_0, v.	Velocity constant, k
0.6803	0.214	1.00	0.7029	0.0027
.6897	.417	1.11	.7026	.0026
.6970	.700	1.11	.7023	.0022
.7040	1.12	..	.7023	.0024
.7113	1.83	1.19	.7024	.0021
.7205	3.25	1.22	.7031	.0020
.7330	7.50	1.20	.7033	.0020
		Av. 1.14	Av. 0.7027	Av. 0.0023

p-Methylaminophenol–N-Methyl-quinone-i—he material used was **a** good, colorless commercial grade of the sulfate ("Photol"), crystallized six times from water. Brawn samples of the material which are offered under the name "Metol" appeared to contain a catalytically active impurity which is not easily removed. The catalyst does not affect the potentials to any noticeable extent, but it greatly accelerates the rate of decomposition of the oxidant. Three crystallizations yielded a colorless product which showed a reaction rate which was less than that for the crude material but still almost twice as great as for the purest samples which we studied.

The results for this system are summarized in Tables VI and VII. They require little comment, for the behavior was quite similar to that already

TABLE VI

VARIATION OF THE POTENTIAL OF THE SYSTEM *p*-METHYLAMINOPHENOL N-METHYLQUINONE-IMINE WITH HYDROGEN-ION CONCENTRATION

P_H[11]	Hydrogen elect. potential, E_h, v.	Constant, C, of Eq. 5	Potential when [Oxid] = [Red], E_n, v.	Av. error, mv.	Calcd., En, v.	Diff. En (Found—calcd.), mv.	Velocity constant, k, when [Oxid]/[Red] = 0.3	3.3
1.10	−0.0648	1.00	0.6813	0.3	0.6820	−0.7	0.0017	0.0020
1.47	.0868	1.00	.6601	.3	.6600	.1	.0018	.0020
2.69	.1589	1.00	.5880	.3	.5879	.1	.0024	.0030
3.56	.2108	1.23	.5361	.3	.5312	4.9	.0020	.0030
3.88	.2296	1.25	.5144	.7	.5087	5.7	.0016	.0026
4.32	.2558	1.16	.4749	.8	.4758	−0.9	.0006	.0008
4.91	.2903	1.11	.4236	.3	.4267	−3.1	.0004	.0005
5.56	.3290	1.27	.3736	.1	.3733	0.3	.0005	.0005
5.88	.3481	1.27	.3498	.5	.3487	1.2	.0011	.0010
6.07	.3589	1.11	.3350	.3	.3354	−0.4	.0010	.0007
6.25	.3694	1.11	.3212	.3	.3230	−1.8	.0004	.0008
6.58	.3891	1.16	.2994	.5	.3010	−1.6	.0014	.0010
6.96	.4114	1.10	.2763	.3	.2773	−1.0	.0014	.0011
7.57	.4475	1.23	.2405	1.0	.2405	0.0	.0013	.0011

$E_0 = 0.6877$ $K_0 = 1.0 \times 10^{-10}$ $K_r = 1.0 \times 10^{-8}$

TABLE VII

THE SYSTEM *p*-METHYLAMINOPHENOL–N-METHYL-QUINONE-IMINE, IN NEUTRAL ALCOHOLIC SOLUTION

Initial potential, E_i, v.	$\frac{[Oxid]}{[Red]}$	Const., C, of Eq. 5	Normal potential, E_0, v.	Velocity constant, k
0.6685	0.187	1.14	0.6935	0.0003
.6777	.357	1.16	.6931	.0003
.6848	.383	1.19	.6929	.0002
.6916	.900		.6931	.0002
.6980	1.37	1.22	.6932	.0002
.7046	2.16	1.10	.6923	.0002
.7134	3.75	1.21	.6936	.0002
.7254	8.50	1.18	.6933	.0002
		Av. 1.17	Av. 0.6931	

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[11] The buffer solutions were similar to those described in Table III.

described. In the first two series of experiments of Table VI it was necessary to correct for incomplete interaction between the molybdicyanide and the reductant in the manner explained above. It is perhaps significant that the values for the constant, C, indicate that the slight association between oxidant and reductant noted in the neutral solutions vanishes in the more strongly acid region. No precipitate was formed as the result of the oxidations; the color produced varied from yellow at *P*H 1.10–3.56 to a purple-red at higher PH values.

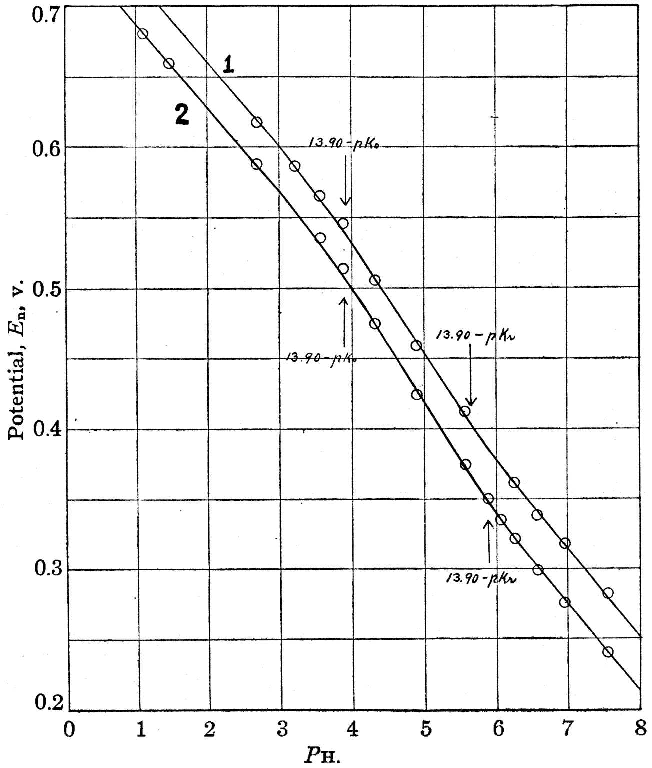

Fig. 4.—Relationship between PH and the potential of half-oxidation. 1, *p*-aminophenol; 2, methyl-*p*-aminophenol.

In spite of the low rate of decomposition of solutions containing N-methyl-quinone-imine, and the greater accuracy which this fact implies, the potentials found do not fit the "best curve" quite as well as in the above instance, as the calculations in the table and the graph of the theoretical equation given in Fig. 4 will show. In constructing this curve consideration was given to the fact that the two "0.06 slopes" are quite sharply defined, and the burden of the error was thus thrown onto the potentials in the intermediate regions.

p-Aminophenol–Quinone-imine.—A good grade of p-aminophenol was distilled at atmospheric pressure in an atmosphere of nitrogen and crystallized from alcohol. Tables VIII and IX summarize the results.

The exceedingly rapid decomposition of this system is evident from the velocity constants of Table VIII, which represent the drop in potential per minute. A preliminary study in a few buffers in the PH range 2–8 at first led us to believe that satisfactory results could only be obtained by the present method in neutral solution. At PH 7.57 the rate of change in the potential is no greater than for the system from p-benzylaminophenol, and the reaction follows the monomolecular course for about three minutes, thus permitting twelve readings for the extrapolation to each initial potential. At PH 6.96 the reaction velocity has more than doubled, but there is still a considerable straight portion of the time-potential curve, and there is little difficulty in obtaining reproducible results. In some of the more acid buffers, however, the situation becomes critical. With the potential changing more than one millivolt per second, one can still make fairly accurate settings of the potentiometer but one is seriously hampered by the fact that the time–potential curve drawn through the first few fifteen-second readings often contains no initial straight portion, the velocity decreasing progressively with time. Some of the curves resembled those calculated for a bimolecular reaction, but the reaction does not appear to be of the second order, for the velocity was not altered by a wide change in concentration.

TABLE VIII

VARIATION OF THE POTENTIAL OF THE SYSTEM p-AMINOPHENOL–QUINONE-IMINE WITH HYDROGEN-ION CONCENTRATION

PH	Hydrogen elect. potential, E_h, v.	Constant, C, of Eq. 5	Potential when [Oxid] = [Red], E_n, v.	Av. error. mv.	Calcd., E_n, v.	Diff., En (Found—calcd.), mv.	Velocity constant. k, when [Oxid]/[Red] = 0.3	3.3
2.69	0.1589	1.24	0.6180	0.8	0.6220	−4.0	0.080	0.103
3.22	.1903	1.26	.5870	.7	.5865	0.5	.082	.090
3.56	.2108	1.26	.5662	.8	.5637	2.5	.072	.080
3.88	.2296	1.21	.5437	1.2	.5414	2.3	.074	.063
4.32	.2558	1.15	.5059	0.8	.5078	−1.9	.046	.030
4.91	.2903	1.13	.4585	.7	.4604	−1.9	.060	.025
5.56	.3290	1.03	.4118	.8	.4089	2.9	...	.032
6.25	.3694	1.47	.3615	.5	.3614	0.1	.080	.041
6.58	.3891	1.24	.3382	.7	.3408	−2.6	.047	.032
6.96	.4114	1.10	.3176	.3	.3172	0.4	.023	.017
7.57	.4475	1.09	.2820	.4	.2807	1.3	.008	.007

$E_0 = 0.7280$ $K_0 = 1.05 \times 10^{-10}$ $K_r = 5.62 \times 10^{-9}$

We did note one encouraging feature of this system, namely, that there is very seldom any lag in the adjustment of the potential at the start of an experiment. This, together with the fact that the reaction appears by one rational criterion to be monomolecular, led us to a fresh attack of the problem. We suspected that the reason for the rapid decrease in the velocity so often noted is simply that a large proportion of the original quinone-imine has been destroyed by the time the first two or three readings can be made and, consequently, that more reliable results would be obtained with a high rather than a low value for the ratio [Oxid]/[Red]. One is usually faced with a greater lag in the potential under these conditions, but the present system is particularly favorable in this one respect. Our new experiments, in which particular weight was given to the experiments where the oxidant was in excess of the reductant, supported this view of the reaction. It was often observed that with a high value of R four or five of the first fifteen-second readings fell on a straight line and thus permitted an accurate extrapolation, while when R was given a low value the velocity was less at forty-five seconds than at thirty seconds. There is no way of telling whether the velocity also decreases during the first thirty seconds, but, as an experiment, we made extrapolations from the first two readings and found the results to be in agreement with the other, surer ones. The results of this type of extrapolation, however dubious in principle, usually have been included in the averages as furnishing some slight support for the none too certain characterization of the system.

Though when viewed individually some of the experiments appear questionable, it is not only true that fairly good agreement is found in the values for the potential at half-oxidation from a given series of experiments, but it will also be apparent that the complete set of results, viewed as a whole, forms a remarkably consistent picture. This can best be seen by examining Fig. 4, Curve I. There can be little question about the essential accuracy of the figure for E_n at P_H 7.57, and the value at P_H 6.96 is nearly as certain. In the next two buffers the potentials measured were shifting with extreme rapidity and the extrapolation curves were short, but the four E_n values found form a good, straight-line curve with the characteristic "0.06 slope." In fact the whole of the E_n-P_H curve conforms closely to the type which has been noted for related compounds. The occurrence of the two "0.06 slopes" connected by the "0.09 slope" could hardly be fortuitous, and we thus feel that there is justification for regarding the constants found for this highly unstable system as fairly close approximations (see Table VIII).[12] Entirely independent support of this conclusion is furnished by the comparison of Veley's value for the basic dissociation constant of *p*-aminophenol[13] with the value here deduced. By a colori-

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[12] Equation 12 was used in making the calculations in the table. It should be noted that Conant and Pratt[4] made use of an equation for the system under discussion which can now be declared incorrect, for it takes no account of the basic dissociation of the oxidant. Our own equation is limited, for by definition it does not hold for solutions of such a P_H that acidic ionization of the reductant takes place.

[13] Veley, J. Chem. *Soc.*, 93, 2122 (1908).

metric method, Veley obtained 6.6 X 10^{-9} at 15°; the value here reported is 5.6 X 10^{-9} at 25°.

From Table **IX** it will be seen that the decomposition of quinone-imine in alcoholic solution is very much slower than in water, and that the rate of the reaction remains very nearly constant over a wide change of concentration. At the end of the experiments in the alcoholic buffer the solution was orange up to the end-point, then yellow. In aqueous solution the color varied from a very pale purple at PH 2.69 to red at PH 4.91, while from PH 5.56 to **7.57** a brown precipitate was formed until up to the point where the end of the titration had been reached.

TABLE IX

THE SYSTEM *p*-AMINOPHENOL–QUINONE-IMINE IN NEUTRAL ALCOHOLIC SOLUTION

Initial potential, Ei, v.	[Oxid]/[Red]	Constant, C, of Eq. 6	Normal potential, E_0, v.	Velocity constant, k
0.7089	0.190	1.12	0.7331	0.0027
.7172	.362	1.19	.7320	.0024
.7250	.593	1.15	.7326	.0023
.7381	1.51	1.02	.7321	.0022
.7443	2.24	1.13	.7326	.0021
7535	3.95	1.18	.7334	0020
.7663	9.44	1.17	.7335	.0020
		Av. 1.14	Av. 0.7329	Av. 0.0022

_p_-Phenylenediamine–Quinonedi-imine.—In aqueous solution this system was less stable than that just described. We had no success with measurements attempted in solutions less acid than PH 5, and no PH region was discovered in which altogether reliable results could be obtained. There is thus little means of determining the accuracy of the few determinations which we were able to make. In view of the use of this system as an oxidation–reduction indicator, these results are reported in Table X; they probably give at least a rough idea of the true potential in the range indicated. There is a suggestion in the results that the E_n–PH curve has the "0.06 slope," for the sum ($E_n - E_h$) approximates a constant quantity;

TABLE X

VARIATION OF THE POTENTIAL OF THE SYSTEM *p*-PHENYLENEDIAMINE–QUINONEDI-IMINE WITH HYDROGEN-ION CONCENTRATION

PH	Hydrogen elect. potential, E_h, v	Potential when [Oxid] = [Red], En, v.	Constant C, of Eq. 5	$E_n - E_h$, v.	Velocity constant, *k* when [Oxid]/[Red] = 0.3	3.3
2.69	0.1589	0.6422	1.00	0.8011	0.084	0.104
3.56	.2108	.5859	1.68	.7967	.059	.086
3.88	2296	.5665	1.74	.7961	.060	.060
4.32	.2558	.5491	2.04	.8049	.046	.058
4 91	.2903	5147	2 08	8050	.074	.090

but we do not feel justified in undertaking a theoretical analysis on the basis of such scanty information.

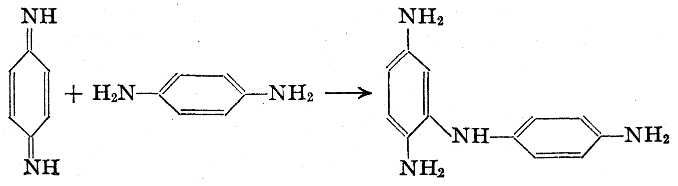
The behavior of the system in alcoholic solution was entirely different, and we are treading on much safer ground in considering the results listed in Table XI. The decomposition was not over-rapid and the time–potential curve was accurately linear up to from one and one-quarter to one and one-half minutes. The normal potential obtained is thus regarded as wholly reliable. The most interesting feature of the results is that the velocity of the destruction of the quinonedi-imine increases steadily as the concentration of the reactant decreases. The drop in potential varies from *25.5* mv. to *6.5* mv. per minute (next to last column) and the direction of the change is particularly striking. It must mean that the reductant enters into the reaction whose rate is measured and that it is the concentration of this component of the system which causes the observed effect. But experimentation showed that the concentration of the reductant is not altered as a result of the decomposition reaction. This was ascertained by performing what amounts to a titration of the reductant remaining after the decomposition reaction had run its course.

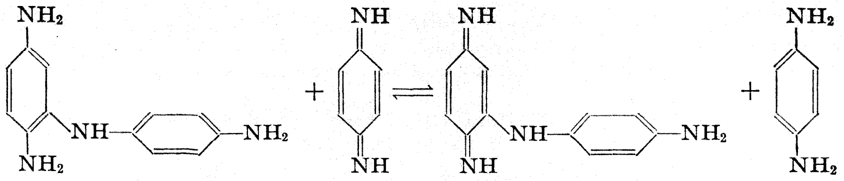
TABLE XI

THE SYSTEM *p*-PHENYLENEDIAMINE–QUINONEDI-IMINE IN NEUTRAL ALCOHOLIC SOLUTION

Initial potential, Ei, v.	$\frac{[\text{Oxid}]}{[\text{Red}]}$	Constant, C, of Eq. 5	Normal potential, E_0, v.	$\frac{E_i - E_t}{t}$	Velocity constant, $k \times 10^{-3}$
0.7586	0.197	1.15	0.7836	0.0255	1.9
.7681	.379	1.16	.7830	.0232	1.9
.7751	.625	1.25	.7823	.0201	2.0
.7820	.978	..	.7824	.0170	2.0
.7900	1.53	1.34	.7834	.0150	2.3
.7968	2.50	1.20	.7826	.0109	2.3
.8061	4.68	1.23	.7823	.0065	2.2
		Av. 1.20	Av. 0.7828		Av. 2.1

Among the various types of reactions by which quinonedi-imine conceivably might be destroyed, there is one which perfectly answers the requirements which the experiments seem to imply, namely, an interaction between the oxidant and the reductant without causing a change in the concentration of the latter. That reaction is the 1,4-addition of the reductant to the oxidant, as follows





From the general knowledge of substituted and unsubstituted quinones, one can say that the equilibrium point of the second reaction would be such as to favor the products almost exclusively, so that the net result of the initial addition reaction, which would be the slower of the two, would be the destruction of two molecules of quinonedi-imine and the maintenance of the reductant at its original concentration. The reaction may, and probably does, go farther, with the ultimate conversion of three molecules of quinonedi-imine into one molecule of a dianilino-quinonedi-imine, but this would not alter the nature of the reaction.

If this mechanism is correct the reaction is of the second order and the reductant functions as a catalyst. The velocity constant may be represented thus

$$k' = \frac{2.3026}{t\,[\text{Red}]_c} \log \frac{[\text{Oxid}]_i}{[\text{Oxid}]_i - x} \tag{16}$$

where $[\text{Oxid}]_i$ is the initial concentration of the quinonedi-imine and where the subscript c indicates a concentration which may be varied from one experiment to another, but which remains unaltered as a result of the reaction. The potential at any time, E_t, may be expressed as follows

$$E_t = E_i - 0.02957 \log \frac{[\text{Oxid}]_i}{[\text{Oxid}]_i - x} \tag{17}$$

Combining Equations 16 and 17 it is seen that

$$k' = 77.87\,(E_i - E_t)/t[\text{Red}]_c \tag{18}$$

This equation calls for a linear time–potential curve for each ratio of oxidant to reductant, but a decreasing velocity with an increase in that ratio. From this equation (and the value 0.0013 M for the total concentration of the organic system in all of the experiments) values for the bimolecular reaction constant have been calculated and they are included in Table XI (last column). The concordance in the values is sufficient to show that the reaction is of the type defined.

Methyl p-Phenylenediamine–N-Methyl-quinonedi-im.—The substitution of a methyl group for one of the amino hydrogen atoms of *p*-phenylenediamine produces little change in the character of the oxidation–reduction system. Measurements in aqueous solution were not very satisfactory and will not be reported. In the alcoholic buffer the decomposition reaction again appeared to be bimolecular, with the reductant functioning as a catalyst, and Equation 18 was thus used in calculating the velocity constants given in Table XII.

TABLE XII

THE SYSTEM METHYL *p*-PHENYLENEDIAMINE–N-METHYLQUINONEDI-IMINE IN NEUTRAL ALCOHOLIC SOLUTION

Initial potential, E_i, v.	$\frac{[\text{Oxid}]}{[\text{Red}]}$	Const., C, of Eq. 5	Normal potential, E_0, v.	$\frac{E_i - E_t}{t}$	Velocity constant, $k' \times 10^3$
0.7230	0.195	1.34	0.7506	0.0213	1.5
.7347	.373	1.34	.7508	.0220	1.9
.7430	.613	1.28	.7513	.0200	1.9
.7502	.957	..	.7512	.0170	2.0
.7572	1.49	1.20	.7505	.0138	2.1
.7661	2.41	1.30	.7508	.0114	2.3
.7759	4.41	1.36	.7508	.0094	3.0
		Av. 1.32	Av. 0.7509		Av. 2.1

***p,p*′-Dihydroxystilbene–Stilbenequinone.**—Owing to the lack of sufficient solubility, this system could not be studied in aqueous solution, but good results were obtained in the alcoholic buffer. The time–potential curve was linear up to about three minutes, but there usually was a lag of from one-half to one minute. The velocity of decomposition again increases with increasing concentrations of the reductant (Table XIII) and the constancy of the velocity constant calculated for the catalytic second order reaction is as good as could be expected.

TABLE XIII

THE SYSTEM *p,p*′-DIHYDROXYSTILBENE–STILBENEQUINONE IN NEUTRAL ALCOHOLIC SOLUTION

Initial potential, E_i, v.	$\frac{[\text{Oxid}]}{[\text{Red}]}$	Const., C, of Eq. 5	Normal potential, E_0, v.	$\frac{E_i - E_t}{t}$	Velocity constant. $k' \times 10^3$
0.8205	0.158	1.37	0.8554	0.0140	0.097
.8310	.294	1.42	.8542	.0124	.096
.8384	.467	1.53	.8528	.0108	.095
.8470	.692	1.36	.8540	.0096	.097
.8535	1.00	..	.8535	.0073	.088
.8611	1.44	1.63	.8541	.0059	.087
.8690	2.14	1.51	.8546	.0045	.085
.8774	6.33	1.53	.8542	.0019	.084
.908	10.0	..	...	.0015	.099
		Av. 1.48	Av. 0.8541		Av. 0.092

According to the interpretation given above of the nature of this type of reaction, this indicates that stilbenequinone forms an addition product with its reduction product, a behavior which appears to be common enough with the quinonedi-imines, but which is unique in the quinone series. It was noted that a bright yellow substance precipitated from the partially oxidized solutions, but failed to form when the reductant was no longer present. It seems probable that this is the quinone formed on oxidation of the primary addition product. The marked additive power of stilbenequinone has been noted by Zincke and Münch,[14] but little is known about the products formed.

p,p'-**Dihydroxydiphenyl–Diphenoquinone.**—The potentials observed for this system exhibited the linear relationship up to about three minutes, and there was usually a delay of one-half minute before the regular descent started. The rate of the reaction showed no variation with a change in the concentrations of oxidant and reductant. A brown substance precipitated from the partially oxidized solutions but not when oxidation was complete. This suggests that the reductant is in some way involved in the decomposition reaction, but the exact nature of the reaction is not clear.

TABLE XIV

THE SYSTEM *p,p'*-DIHYDROXYDIPHENYL–DIPHENOQUINONE IN NEUTRAL ALCOHOLIC SOLUTION

Initial potential, E_i, v.	$\frac{[\text{Oxid}]}{[\text{Red}]}$	Const., C, of Eq. 6	Normal potential, E_0, v.	Velocity constant, k
0.9326	0.197	1.04	0.9550	0.0059
.9410	.379	1.06	.9544	.0066
.9480	.625	1.05	.9544	.0061
.9538	.978		.9541	.0060
.9605	1.53	1.14	.9546	.0050
.9670	2.50	1.08	.9543	.0050
.9780	4.68	1.20	(.9566)	.0048
		Av. 1.08	Av. 0.9544	Av. 0.0056

Other Systems.—Oxidation experiments in the neutral alcoholic buffer solution with the following compounds were unsuccessful; the solutions were so unstable that the potentials could not be determined accurately by the present method: o-aminophenol, o-phenylenediamine, catechol, nitrohydroquinone, 2,6-dihydroxynaphthalene.

One of the purposes of this investigation was to acquire information and experience of various unstable systems which might be useful in a study of the oxidation–reduction systems which are formed when monatomic phenols and amines are oxidized. One or two such systems appear to possess a stability well above the average, and it was hoped that some such system might be discovered which would prove accessible to direct potential measurement. We have made a preliminary study by the method here described of 9-chloro-10-phenanthrol and the radical produced when it is oxidized,[15] and we have found that the system is electromotively active and that it behaves in much the same way as those which have been described above. The potentials, however, appear to be subject to a peculiar fluctuation from one experiment to another, and only a thorough investigation can determine if it is possible to characterize such systems by direct methods.

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[14] *Zincke and* Münch, *Ann.*, 335, 167 (1904).

[15] *Goldschmidt and Steigerwald, ibid.*, 438, 202 (1924).

Comparison of Results

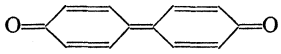
Table XV lists the rounded average values found for the normal potentials of the systems studied. This term is defined as the potential difference between a dilute solution of equimolecular quantities of the oxidant and the reductant when neither is ionized, and a hydrogen electrode in the same solvent.

TABLE XV

ROUNDED AVERAGE VALUES

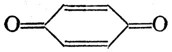
System named as reductant	Normal potential, E_0 Alcohol, v.	Normal potential, E_0 Water, v.	Half-life (neutral solution) Alcohol, min.	Half-life (neutral solution) Water, min.
p-Methylaminophenol	0.693	0.688	35.6	7.4
p-Benzylaminophenol	.703	.698	3.9	1.4
p-Aminophenol	.733	.728	3.9	1.1
p,p'-Dihydroxydiphenyl	.954	..	1.6	...
p,p'-Dihydroxystilbene	.854	..	1.1	...
p-Phenylenediamine	.783	(.801)	0.5	0.1
N-Methyl-p-phenylenediamine	.751	..	.5	...

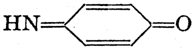
The potential of diphenoquinone (I) and its reduction product is the highest yet recorded for an organic system. Stilbenequinone (II), though it has a more extended conjugated system of linkages, falls well below this compound in potential, though it is about equal to the polyhalogenated o-benzoquinones and **0.15** v. above *p*-benzoquinone on the potential scale.

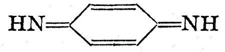

I


II

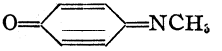
Comparison of the various quinone-imines and di-imines (in alcoholic solution) with quinone shows that the substitution of the imino group for the ketonic oxygen atom progressively increases the affinity of the quinonoid substance for hydrogen

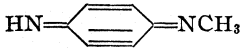

$E_0 = 0.715$ v.


$E_0 = 0.733$ v.


$E_0 = 0.783$ v.

The N-methyl derivatives of quinone-imine and quinonedi-imine are lower in potential than the parent substances by about the same amount


$E_0 = 0.693$ v.


$E_0 = 0.751$ v.

A benzyl group has much the same effect as methyl.

A further interesting comparison is of the basic dissociation constants determined for three of the systems, and these are listed in Table XVI, along with the *pK*-values ($pK = -\log K$). We have also included in the table the data of Clark, Cohen and Gibbs for the first dissociation constants at 30° which they report for systems studied by them.

TABLE XVI

FIRST BASIC DISSOCIATION CONSTANTS

System, named as reductant	Reductant K_r	pK_r	Oxidant K_o	pK_o
p-Aminophenol	5.6×10^{-9}	8.2	1.0×10^{-10}	10.0
p-Methylaminophenol	1.0×10^{-8}	8.0	1.0×10^{-10}	10.0
p-Benzylaminophenol	1.5×10^{-9}	8.8	9.0×10^{-12}	11.1
p-Aminodimethylaniline[2]	3.9×10^{-8}	7.4	5.0×10^{-7}	6.3
o-Tolidine[2]	6.2×10^{-10}	9.2	2.7×10^{-8}	7.6

According to the present results the ionization constants for *p*-aminophenol and quinone-imine are not appreciably affected by the substitution of methyl for hydrogen, but they are both decreased by the substitution of a benzyl group. The difference between pK_0 and pK_r is fairly constant, from 1.3 to 2.2 units, and it is always in the same direction. The quinone-imine in each case has a smaller dissociation constant than its reduction product. It appears odd that in the case of the di-imines it is the oxidant which is the more highly ionized. This causes an interesting difference in the form of the E_n–P_H curves, a difference at once apparent on comparing Clark's curves with those given here.

In Table XV the systems have been listed in the order of decreasing stability. As an arbitrary basis of comparison in aqueous solution, we have taken the rates of decomposition at P_H 7.57. The half-life periods given are fairly accurate for the alcoholic solutions; for water they represent approximations. The most striking feature about these results is that the systems are all far more stable in a neutral phosphate solution when this contains 37% of alcohol than when it contains no other solvent but water. We see no way of accounting for this, but the practical implications are obvious. If a given system proves too unstable for potentiometric study in aqueous solution it is likely that the conditions will be improved on operating in a partially non-aqueous solvent. Not only is the stability greater, but it has been observed throughout this work that the velocity constants found in the various experiments of a series show much the better agreement in the case of the alcoholic solutions.

There appears to be little correlation between the velocity of decomposition and the acidity of the solution; the only marked effect noted is that quinone-imine is decidedly more stable at P_H 7–8 than in more acidic solutions. It is evident that the rate of the reaction often varies considerably according to the nature of the solution and the relative concentrations of oxidant and reductant, and that there is often a great difference in the behavior of closely related compounds.

We can say little regarding the nature of the reactions by which the oxidants suffer decomposition other than that with two quinonedi-imines and one quinone of unusual structure the reaction very probably is one of addition of the reductant to the oxidant. In the other cases there are so many possibilities that velocity measurements alone are of little assistance in establishing the complete mechanisms. It is not improbable that each of the following reactions contributes in some instances to the instability of the systems: self-condensation and self-oxidation of the oxidant, the addition of the elements of water, reaction with the reductant.

Summary

By means of a "discontinuous titration" method it has been possible to determine the oxidation–reduction potentials of systems which are so unstable that the half-life period for the decomposition of the oxidant is of the order of one-tenth to one-half minute. With the systems formed by *p*-aminophenol and two of its N-alkyl derivatives the variation of the potential with the hydrogen-ion concentration has been studied in the PH range 1–8, and the basic dissociation constants have been determined from the results. Seven systems have been studied and the more important constants found are summarized in Tables XV and XVI.

BRYN MAWR, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NORTH CAROLINA]

PRELIMINARY STUDY ON THE ANTIRACHITIC PROPERTIES OF SHRIMP OIL

BY F. P. BROOKS,[1] ROY F. ABERNETHY AND F. C. VILBRANDT[2]

RECEIVED AUGUST 4, 1930 PUBLISHED DECEMBER 18, 1930

Shrimp oil is the ether-soluble oil obtained when the waste of the shrimp industry is extracted. It has been obtained by the authors[3] in their study on the utilization of shrimp waste. A later chemical study of this oil showed the presence of 19% of cholesterol, the presence of which led to the study of the oil for its antirachitic properties.

This investigation consisted in the feeding study of the oil on white rats, which had become rachitic by special feeding. Standard cod liver oil and shrimp oil were fed at the same time to get a relation of the antirachitic properties of the oil. After three generations of breeding, the selected young rats were fed on Sherman's growth diet B consisting of 66.7 g. of whole wheat, 33.3 g. of whole milk and 1.3 g. of sodium chloride, until they were twenty-eight days old. Part of the series was continued on this diet to serve as normal controls, another part was fed Steenbock's diet 2965[4] for the production of rickets. When they had developed the rickets,

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[1] Assistant Professor of Physiological Chemistry, University of North Carolina.

[2] Professor of Chemical Engineering, Iowa State College, Ames, Iowa.

[3] F. C. Vilbrandt and R. F. Abernethy, "Utilization of Shrimp Waste," Fisheries Document 1078 (1930).

[4] H. Steenbock and A. Black, *J. Biol. Chem.*, 64, 268 (1924).

which condition was shown by x-ray pictures and outward appearances, the rachitic rats were divided into three divisions. The first division was fed cod liver oil, the second division was fed shrimp oil and the third division was continued on the rachitic diet. The oils were added to the rachitic diet and the feeding test was continued for a period of five days. There were four groups of rats, (1) the rachitic and (2) the normal rats to serve as extreme controls and the two classes of rats one of which was fed cod liver oil and the other shrimp oil.

In this investigation three methods of measuring the amount of cure in the rats were used: (a) McCollum's[5] line test; (b) percentage of ash in the bone[6] and (c) the amount of calcium and phosphorus in the blood. The line test and the determination of the calcium and phosphorus in the blood were made by Dr. F. P. Brooks. (These data are not available and are material for a separate and more extensive paper by Dr. Brooks.) The ash determinations on the bone and the calcium and phosphorus determinations on the ash were made according to the Standard Methods.[7] The data in Table I and II will show there was some cure by the shrimp oil, but also that there was less cure in the second series than there was in the first.

In the first series of determinations 16 rats were used. At the age of twenty-eight days twelve rats were fed the Steenbock diet 2965 for four weeks. At the end of this time x-ray pictures and the outward appearance showed the animals to be rachitic. After the animals were found to be sufficiently rachitic, four of the twelve were fed shrimp oil with the rachitic diet, four were fed the rachitic diet with cod liver oil added and the other four were fed the rachitic diet. They were fed this oil diet for five days and then the sixteen rats were killed, the blood was taken for analysis and the bones from the rear legs were removed for the line test and the ash determination. The blood from the four rats of one group was combined to get a sufficient quantity for analysis. The bones were preserved in acetone until analyzed.

The Effect of Treated Feeds on **Ash** in Bones.—The results for the rat noted K are abnormal; the amount of food consumed by this rat was small, hence the results on this rat are not taken into consideration in determining the average. Examination of the data will disclose that the rachitic rat had the smallest percentage of ash and the control the highest. The rachitic rats that were fed the oils show some cure by being between the two extremes.

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[5] E. V. McCollum, *J. Biol. Chem.*, 51, 41 (1922).

[6] F. S. Hammett, *ibid.*, 64, 415 (1925).

[7] Bethke, Steenbock and Nelson, *ibid.*, 58, 76 (1923); J. O. Halverson and Olaf Bergeim, "The Preparation of $N/100$ Permanganate Solutions," *J. Ind. Eng. Chem.*, 10, 119 (1918); R. E. G. Mahin. "Quantitative Analysis," 1922, p. 453.

TABLE I

AMOUNT OF ASH IN BONES

Condition of rats	Notation	% Ash	Condition of rats	Notation	% Ash
Rachitic	A	43.55	Cod liver oil fed	I	44.71
Rachitic	B	41.54	Cod liver oil fed	J	44.71
Rachitic	C	45.62	Cod liver oil fed	K	40.00
Rachitic	D	43.61	Cod liver oil fed	L	47.37
Average		43.58	Average		45.59
Shrimp oil fed	E	46.77	Normal controls	M	53.93
Shrimp oil fed	F	45.33	Normal controls	N	54.30
Shrimp oil fed	G	47.65	Normal controls	O	52.47
Shrimp oil fed	H	44.54	Normal controls	P	54.77
Average		46.07	Average		53.82

Effect of Treated Feeds on Calcium and Phosphorus in Bones.—As in the determination of the percentage of the ash, the percentage of the calcium and of the phosphorus shows that the shrimp oil has some curative properties on rachitic rats.

TABLE II

CALCIUM AND PHOSPHORUS CONTENT OF ASH

Condition of rats	Notation	Calcium, % Bone	Calcium, % Ash	Phosphorus, % Bone	Phosphorus, % Ash
Rachitic	A	16.78	38.54	7.81	17.94
Rachitic	B	15.65	37.26	6.64	16.13
Rachitic	C	16.22	37.70	8.43	18.60
Rachitic	D	16.95	38.90	...	
Average		16.40	38.10	7.63	17.56
Shrimp oil	E	18.05	38.59	8.59	18.34
Shrimp oil	F	17.55	38.61	8.30	18.30
Shrimp oil	G	18.14	38.07	9.09	19.08
Shrimp oil	H	16.81	37.80	8.12	18.24
Average		17.64	38.27	8.52	18.49
Cod liver oil	I	17.49	38.83	8.07	18.10
Cod liver oil	J	16.23	38.26	...	...
Cod liver oil	K	15.60	38.90	...	...
Cod liver oil	L	17.45	39.20		...
Average		16.69	38.79	8.07	18.10
Controls	M	20.32	37.64	10.05	18.64
Controls	N	20.11	36.91	9.45	17.23
Controls	O	19.55	37.00	8.65	16.30
Controls	P	20.63	37.85	...	...
Average		20.15	37.35	9.54	17.39

Summary

In the investigation of the antirachitic properties of shrimp oil it was found from the analysis of the blood and the bones that the oil had proper-

ties akin to cod liver oil that tended to cure the rachitic rats. From an examination of the data it is found in the first series that the shrimp oil was as potent as the cod liver oil. The second series showed some cure but less than the cod liver oil, probably due to the increasing rancidity of the shrimp oil.

AMES, IOWA

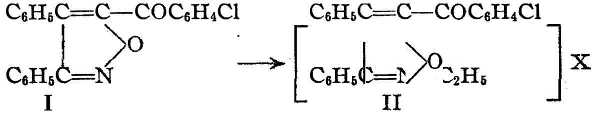
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

PSEUDO BASES IN THE ISOXAZOLE SERIES. THIRD PAPER

BY E. P. KOHLER AND C. L. BICKEL

RECEIVED AUGUST 12, 1930 PUBLISHED DECEMBER 18, 1930

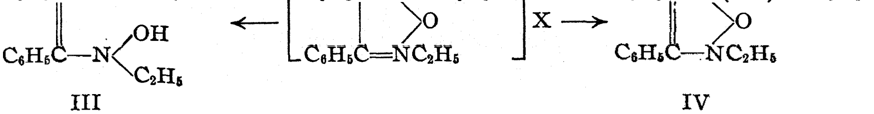
The pseudo bases that have been described in earlier papers of this series are derived from isoxazoles in which all available positions are filled with hydrocarbon residues. In all these cases the rearrangement of the true base results in a pseudo base in which the hydroxyl group occupies the 5-position. In order to determine whether this mode of rearrangement is altered by an acidic group in this position, we have alkylated a ketonic isoxazole and studied the behavior of the resulting salts toward bases



I II

The ethylation presented no difficulties and the salts could be manipulated in the same manner as those described heretofore. When they were shaken at a low temperature with aqueous sodium bicarbonate or sodium hydroxide and ether, the organic material immediately passed from the aqueous to the ethereal layer and when the ethereal solution was acidified the salts were regenerated. The alkylated ketonic isoxazole, therefore, forms a pseudo base in the usual manner.

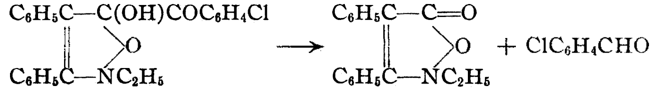
By cautious manipulation of its ethereal solution it was possible to isolate the pseudo base as a colorless crystalline compound. Ozonization of this compound yielded equivalent quantities of benzoic and *p*-chlorobenzoic acids, and a halogen-free substance which has not been identified. This result shows that the rearrangement, as usual in this series, leads to a 5-hydroxy compound, and it leaves but two possible formulas for the pseudo base



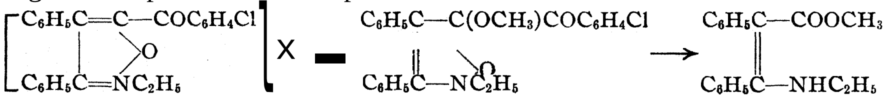
III IV

The lack of color in our pseudo base definitely excludes formula III which represents an α-diketone that would be intensely yellow. The pseudo base, therefore, is constituted precisely like all the others that we have described. It presents, however, certain peculiarities which are due to the substitution of the ketonic group for a hydrocarbon residue. It is not possible, for example, to transform the base into its ether by treatment with alcoholic potassium hydroxide. It is also impossible to secure such an ether directly from the salts. That this difference between the new pseudo base and nearly all others that are known is due to the ketonic group, is shown by the fact that it is equally impossible to methylate the ketonic hydroxy isoxazolines in which the relation between the hydroxyl and ketonic groups is the same.

Another peculiarity of the new pseudo base shows itself in the ease and in the manner in which it alters with time. Other pseudo bases of this series, in solution, and especially in the presence of alkalies, lose water more or less rapidly and pass into open-chained anhydro compounds. The ketonic compound changes spontaneously even in the solid condition and the principal product is ethyl diphenyl isoxazolone

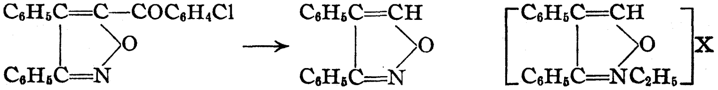


A similar cleavage accounts for some of the difficulties encountered in attempts to prepare the methyl ether directly from the salts. The ether may be formed in the operation but, if so, then it is immediately cleaved and the process goes further than in the spontaneous decomposition, ending in the open-chained compound VI



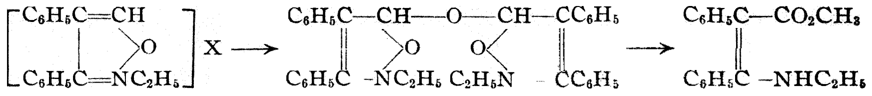
V VI

The open-chained cleavage product may, as has been stated, originate in the methyl ether V, but it is possible also that cleavage precedes methylation. In order to explore this possibility we have also examined the behavior of the salts that are obtained by ethylating 3,4-diphenyl isoxazole. These can be obtained without difficulty by means of a series of reactions which may be represented as follows



VII VIII

In this case neither the pseudo base nor its methyl ether could be isolated. When the salts VIII were treated with aqueous alkalies they immediately yielded a dimolecular anhydride, and when either this anhydride or the salts were acted on by methyl alcoholic sodium hydroxide, the product was the open-chained ester VI



VIII IX VI

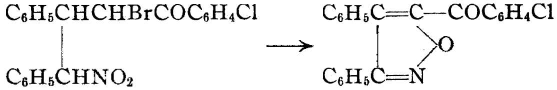
It is evident that the open-chained ester may originate either from the methyl ether V or from an antecedent cleavage product akin to VIII. Its structure is certain because it gives benzoic acid and ethyl benzamide when ozonized, therefore, has a double linkage in the α,β-position, and hydrochloric acid converts it into benzoyl phenyl acetic ester—a characteristic transformation of β-amino unsaturated esters

$$\underset{\text{VI}}{C_6H_5C(NHC_2H_5){=}C(C_6H_5)COOCH_3} \longrightarrow \underset{\text{X}}{C_6H_5COCH(C_6H_5)COOCH_3}$$

The formation of the open-chained ester represents a novel transformation of pseudo bases in the isoxazole series, a transformation which can occur only when the 5-position is unoccupied or is occupied by a group that is easily removed by bases. Since the pseudo bases derived from isoxazoles, in which both the 3- and 5-positions are unoccupied, undergo an entirely different type of rearrangement, this transformation into an open-chained ester may be regarded as a characteristic reaction of pseudo bases derived from 3,4-disubstituted isoxazoles.

Experimental Part

The isozazole that served as a starting point has been described heretofore because it turns up in small quantities whenever the corresponding bromo compound reacts with bases[1]



For preparing it in quantity we devised a method which gives a yield that is almost quantitative. The procedure was as follows.

A suspension of 100 g. of the bromo compound and an equal weight of potassium acetate in 500 cc. of methyl alcohol was boiled until bumping became serious. The mixture was then cooled and filtered. After washing the solid isoxazole with methyl alcohol until it was colorless, the filtrate and washings were boiled again and this operation of boiling and filtering was repeated as often as was necessary until no more solid separated. The filtrate was then concentrated in steps, finally evaporated almost to dryness, and set aside. It deposited a solid cake of isoxazole, bromide and acetate. The salts were removed with water, and the isoxazole washed with ether, which dissolved a green impurity along with a small quantity of the isoxazole. All fractions of the isoxazole were combined and recrystallized from glacial acetic acid. The yield was 77.5 g. or 98%; m. p. 165–166°.

Ethylation.—A suspension of 15 g. of the isoxazole in 50 g. of diethyl sulfate was heated in an oil-bath for two and one half hours at 125–130°. The isoxazole gradually

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[1] Kohler and Addinall, THIS JOURNAL, 52, 1597 (1930).

dissolved during the heating, and the solution became quite brown. This solution was used for preparing the salts represented by II.

The Acid Sulfate.—The ethylation mixture was heated on a steam-bath with 25 cc. of concentrated hydrochloric acid and an equal volume of water until the two layers disappeared. The solution was then extracted with ether, which removed unchanged isoxazole and other impurities and evaporated. It finally deposited colorless plates. which were washed with ether, and with a little water, then recrystallized from methyl alcohol. The salt separated in colorless plates melting at 192–193°.

Anal. Calcd. for $C_{24}H_{20}O_6NClS$: C, 59.3; H, 4.2. Found: C, 59.3; H, 4.6.

The Ferric Chloride Double Salts.—The ethylation mixture was hydrolyzed as before, diluted with 20 cc. of water and thoroughly extracted with ether. The aqueous solution was then heated to expel dissolved ether, cooled and treated with a saturated solution of ferric chloride which was added drop by drop as long as a precipitate formed. The precipitate was washed with ether and a little water, dried and recrystallized from glacial acetic acid, from which it separated in yellow plates. The yield was 18.2 g.

The earlier preparations yielded a salt that melted at 130.5'. Later a new salt melting at 139.5° made its appearance, and after that only the higher-melting salt could be obtained. The composition of the two salts was the same.

Anal. Calcd. for $C_{24}H_{19}O_2NCl_6Fe$: Cl, 24.1. Found: (130") Cl, 23.1; (139°) 23.4.

The Pseudo Base IV.—Inasmuch as the pseudo base decomposes spontaneously it was made only in small quantities as needed. For this purpose 2.25 g. of either of the ferric chloride double salts was suspended in alcohol-free ether and treated with a water solution of 5 g. of sodium bicarbonate. A vigorous reaction occurred and the ether layer immediately became yellow. After removing the ferric hydroxide by filtration the ethereal layer was separated and the aqueous solution extracted with fresh ether. The ethereal solution was dried with sodium sulfate and allowed to evaporate. It deposited a slightly yellow product which became colorless when recrystallized from ether–petroleum ether; yield, 1.3 g., equal to 85%.

Anal. Calcd. for $C_{24}H_{20}O_3NCl$: C, 70.9; H, 5.0. Found: C, 70.5; H, 5.1.

The pseudo base is insoluble in water, soluble in all organic solvents except petroleum ether. It crystallizes in colorless prisms and melts with decomposition at about 128". When its solution in alcohol-free ether is shaken with 1:1 hydrochloric acid and a saturated solution of ferric chloride, it deposits in nearly the calculated quantity the ferric chloride double salt which melts at 139°.

Spontaneous Decomposition.—A 0.5-g. sample of the pseudo base which had been kept in a glass-stoppered bottle for several months and had become dark in color, was dissolved in ether. From the resulting ethereal solution sodium bicarbonate extracted an acid which was identified as 4-chlorobenzoic acid by its melting point and by comparison with a sample on hand. After removing the chloro acid, the ethereal solution was dried, concentrated and diluted with petroleum ether. It thereupon deposited a solid which crystallized in diamond-shaped prisms and melted at 145–146°.

Anal. Calcd. for $C_{17}H_{15}O_2N$: C, 77.0; H, 5.7. Found: C, 77.0; H, 5.7.

The composition, solubility, crystalline form and melting point agree with those of ethyl diphenyl isoxazolone. This substance was, therefore, synthesized by the method of Kohler and Blatt.[2] A comparison of the two products proved their identity.

Ozonization of the Pseudo Base.—A current of ozonized oxygen containing about 6% ozone was passed through a suspension of the pseudo base for one and one-half hours. At the outset the ozone was absorbed freely and the base dissolved. The ethyl bromide

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[2] Kohler and Blatt, THIS JOURNAL, 50, 514 (1928).

was evaporated in a current of dry air, the residual oil shaken with water and the resulting emulsion extracted with ether. From the ethereal solution sodium bicarbonate extracted both benzoic and p-chlorobenzoic acids. The ethereal solution from which these acids had been removed was dried, concentrated and diluted with petroleum ether. It deposited a pale yellow solid melting at 120–130°. As no method was found for purifying the substance it could not be identified.

Attempts to Make a Methyl Ether.—Methyl alcohol containing a trace of potassium hydroxide had no action on the pseudo base and sodium methylate was found to be too destructive. The ferric chloride double salt was, therefore, treated with sodium bicarbonate in the following manner. One gram of the finely powdered double salt was suspended in 25 cc. of methyl alcohol. To this suspension were added 25 g. of ice. 40 cc. of alcohol-free ether and 0.6 g. of sodium bicarbonate dissolved in water. The mixture was shaken until the yellow salt had disappeared. The ethereal layer was then decanted and filtered, and the aqueous layer thrice extracted with ether. The ethereal solutions were dried, concentrated to small volume and diluted with petroleum ether. On cooling and rubbing they deposited 0.4 g. of a colorless solid which melted when crude at 102°. Addition of acid to the aqueous solution precipitated *p*-chlorobenzoic acid.

These same products—p-chlorobenzoic acid and a substance melting at 101–102°—were obtained when 2 g. of the ferric chloride double salt was shaken with 50 cc. of methyl alcohol, 50 g. of ice, 75 cc. of alcohol-free ether, and 2 g. of sodium hydroxide dissolved in water. The yield of the product melting at 101–102° was 0.9 g. or 90%. The product was recrystallized both from ether–petroleum ether and from acetone–methyl alcohol, but the melting point remained the same.

Anal. Calcd. for $C_{18}H_{19}O_2N$: C, 76.9; H, 6.8; OCH_3, 11.05. Found: C, 76.8; H, 6.8; OCH_3, 10.6.

The ester is readily soluble in acetone, moderately soluble in ether and methyl alcohol. It crystallizes in plates.

Methyl α,β-Diphenyl-β-ethylaminocinnamate

Ozonization of the Ester.—Through a solution of 4 g. of the ester in 35 cc. of carbon tetrachloride a rapid current of ozonized oxygen was passed for one and one-half hours—half an hour after ozone appeared in the effluent gas. The solvent was pumped off and the residual oil shaken with ice water. The resulting emulsion was heated gently, the temperature being kept below 50°, then cooled and extracted with ether. The ethereal solution contained benzoic acid, which was removed with bicarbonate and identified.

After removal of the benzoic acid, the ethereal solution was dried with sodium sulfate and evaporated. It left an oil which solidified after vigorous rubbing. By recrystalliiation from ether–petroleum ether the solid was obtained in diamond-shaped plates which melted at 68–69°.

Anal. Calcd. for $C_9H_{11}ON$: C, 72.4; H, 7.5. Found: C, 72.5; H, 7.6.

The composition of the substance corresponds to that of ethyl benzamide, and it gave benzoic acid when it was boiled with concentrated hydrochloric acid, but owing to the small quantity available ethylamine could not be identified with certainty. Ethyl benzamide was therefore prepared from benzoyl chloride and ethylamine. It melted at 68–69° and a mixture of the preparation and the ozonization product melted at the same temperature.

Hydrolysis of the Ester.—A solution of 0.55 g. of the ester in concentrated hydrochloric acid was set aside for a day. On dilution with an equal volume of water it deposited a solid which was identified as desoxybenzoin. The diluted solution on standing deposited more solid, which proved to be a mixture. It was separated by fractional crystallization from ether–petroleum ether into desoxybenzoin and a substance which melted at 72–73°.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.6; H, 5.6; Found: C, 75.3; H, 5.7.

This substance was identified as the methyl ester of benzoyl phenyl acetic acid by comparison with a sample on hand.[3] Concentrated hydrochloric acid gradually transformed it into desoxybenzoin.

Preparation of 3,4-Diphenyl Isoxazole (VII).—The preparation of this isoxazole from anisoyl diphenyl isoxazole was described in an earlier paper.[4] We obtained it in a much better yield from *p*-chloro-benzoyl diphenyl isoxazole. Since it is readily cleaved, it is necessary to operate as rapidly as possible and it is advantageous to operate with small quantities. Our procedure was as follows. A suspension of 2 g. of 3,4-diphenyl-5-(p-chloro-benzoyl)-isoxazole in 20 cc. of ethyl alcohol, and a solution of 0.5 g. of sodium hydroxide in 10 cc. of ethyl alcohol, were mixed at the boiling point. The mixture was boiled for one and one-half minutes, during which the isoxazole dissolved, then immediately cooled under the tap and filtered, to remove a small quantity of unchanged material. The filtrate was diluted with 150 cc. of water and set aside for thirty minutes, during which it deposited the diphenyl isoxazole. The yield of product was 1.15 g. or 98%, and approximately 0.1 g. of starting material was recovered.

Ethylation.—A suspension of 3.45 g. of diphenyl isoxazole in 5.0 g. of ethyl sulfate was heated in an oil-bath to 110° for four hours. The resulting light brown solution was heated on a steam-bath with 3 cc. of concentrated hydrochloric acid and 3 cc. of water until the mixture became homogeneous. The solution was then diluted with 3 cc of water, cooled and extracted with ether. The aqueous layer was heated to expel all of the ether, cooled and treated very gradually with excess of saturated ferric chloride solution.

The ferric chloride double salt is uncommonly low-melting, and when it is precipitated rapidly or in the presence of ether it tends to separate as an oil exceedingly difficult to solidify. When no crystals are available for inoculation the ferric chloride should be added a few drops at a time until vigorous scratching of the walls of the vessel starts crystallization. The salt was recrystallized from glacial acetic acid and petroleum ether. It is readily soluble in glacial acetic acid and in methyl alcohol, sparingly soluble in water, almost insoluble in ether and petroleum ether. It crystallizes in pale yellow plates and melts at 75–76°. The yield was 97%.

Anal. Calcd for $C_{17}H_{16}ONCl_4Fe$: C, 45.5; H, 3.6. Found: C, 45.2; H. 3.9.

Action of Bases on the Salt: The Dimolecular Anhydride (IX).—The usual method of obtaining pseudo bases by shaking the salts with sodium hydroxide in the presence of ether was inapplicable in this case because extraction is too slow and the product is rapidly decomposed by the hydroxide. When benzene was substituted for the ether the result was more satisfactory. Thus one gram of the salt was shaken with 10 cc. of benzene and one gram of sodium hydroxide in 20 g. of ice and water until all of the salt was decomposed. The benzene layer was then decanted, dried and evaporated. It left a solid which was recrystallized from benzene and ether. It separated in colorless prisms melting at 148°.

Anal. Calcd. for $C_{34}H_{32}O_3N$: C, 79.0; H, 6.2; mol. wt., 516. Found: C, 79.0; H. 6.2; mol. wt., 488.

Ozonization.—A solution of 0.7 g. of the substance in 10 cc. of carbon tetrachloride was ozonized for forty-five minutes. The solvent was pumped off and the residual oil shaken with ice water in the usual manner, but the water solution was treated directly

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[3] Kohler, THIS JOURNAL, 46, 1742 (1924).

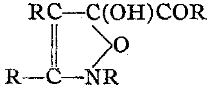
[4] Kohler and Davis, *ibid.*, 52, 4527 (1930).

with phenylhydrazine hydrochloride. A yellow precipitate formed which was identified as the phenylhydrazone of phenyl glyoxylic acid by comparison with an authentic sample.

Cleavage of Bases.—A solution of a small quantity of the dimolecular compound in methyl alcohol containing a trace of sodium hydroxide was boiled down, cooled and diluted with water. It deposited the unsaturated amino ester VI. The filtrates from the ester later also deposited a small quantity of desoxybenzoin. This unsaturated amino ester was obtained also when the ferric chloride double salt was shaken with ice and methyl alcoholic sodium hydroxide. In this case the yield of ester was 82%.

Summary

1. In the pseudo bases which are formed from isoxazolinium salts that are completely substituted and have an acidic group in the 5-position, the hydroxyl group occupies the 5-position:



Owing to the ease with which they are cleaved, their behavior is quite different from that of the pseudo bases derived from other tri-substituted isoxazoles.

2. The pseudo bases derived from β,γ-diphenyl isoxazole likewise have an hydroxyl group in the 5-position. They undergo a characteristic rearrangement into open-chained compounds.

Converse Memorial Laboratory
Cambridge, Massachusetts

[Contribution from the Chemical Laboratory of Iowa State College]

THE INFLUENCE OF ACID CHLORIDES AND OF PYRROLE ON THE COLOR TEST FOR REACTIVE ORGANOMETALLIC COMPOUNDS. THE CONSTITUTION OF PYRRYLMAGNESIUM HALIDES

By Henry Gilman and Lloyd L. Heck

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Introduction

In continuation of studies[1] on the reaction between acid halides and the Grignard reagent, it was noted that some acid chlorides appeared to interfere with the sensitive color test[2] for reactive organometallic compounds. This prompted an investigation of the effect of several typical acid halides on the color test. It has been found that such interference is not general.

Fortunately, the occasional interference of acid halides need not be of serious consequence for several reasons. First, the reaction between RMgX

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[1] Gilman, Fothergill and Parker, *Rec. trav. chim.*, *48*, 748 (1929); Gilman and Fothergill, This Journal, 51, 3501 (1929).

[2] (a) Gilman and Schulze, *ibid.*, **47**, 2002 (1925); (b) Gilman and Schulze, Bull. *soc. chim.*, *[4]* **41**, 1479 (1927); (c) Gilman and Heck, *Rec. trav. chim.*, *48*, 193 (1929); (d) Gilman and Heck, *Ber.*, 62, 1379 (1929); (e) Gilman, Sweeney and Heck, This Journal, 52, 1604 (1930); and (f) Gilman and Heck, *Rec. trav. chim.*, *49*, 218 (1930).

compounds and acid halides is rapid.[3] Second, it is possible to use equivalent quantities of acid halide and Grignard reagent, the former being weighed out and the latter titrated before use. Third, in reactions involving alkylmagnesium halides having an alkyl group of low weight, it is possible to detect a slight excess of such an RMgX compound by observing the evolution of gas when a small sample of the reaction mixture is removed and hydrolyzed.

However, in a very special and rarely met with case there is another source of interference with some acid halides. Such interference might arise when a part or all of the commonly used diethyl ether is replaced by an amine like dimethylaniline.[4] Amines of this type may give, in some cases, products with acid halides whose color might interfere with the colors developed in testing for reactive organometallic compounds.[5] These are considered in the "Experimental Part."

We have had occasion to test the reliability of the color reaction with an unusually comprehensive and varied series of compounds. In addition to the occasional interference of acid halides, we directed attention recently[2'] to the infrequent interference of a few amino compounds by the production of colors which obscure those otherwise normally developed. The peculiar effects of pyrrole are of considerable interest in connection with the constitution of pyrrylmagnesium halides. It is known that when an RMgX compound reacts with a compound containing active hydrogen, the hydrogen is replaced by the –MgX group. Accordingly, the structure of a pyrrylmagnesium halide should be that represented by Formula (A). However, pyrrylmagnesium halides give reaction products which generally have the new grouping attached to carbon and not to nitrogen, and most frequently attached to an α-carbon atom. Consequently, a question has been raised[6] concerning the possibility of such types having Formula (B), either prior to or during its reaction with other compounds like carbon dioxide.

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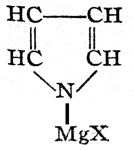
[3] See Gilman, Heck and St. John, *Rec. trav. chim.*, 49, 212 (1930), for the relative rates of some reactions involving organomagnesium halides. Obviously, the rate of reaction might be affected considerably in some cases by steric influences of groups about the acid halide grouping.

[4] See Gilman and McCracken, *ibid.*, 46, 463 (1927), for the effect of some solvents on the yields of Grignard reagents.

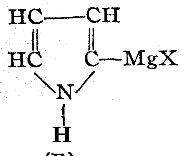
[5] Michler, *Ber.*, 9, 716 (1876); Michler and Dupertuis, *ibid.*, 9, 1899 (1876); Michler and Gradmann, *ibid.*, 9, 1912 (1876); Michler and Moro, *ibid.*, 12, 1168 (1879); Michler and Meyer, *ibid.*, 12, 1791 (1879); Staudinger and Stockmann, *ibid.*, 42, 3485 *(1909).* Some references to colored products from Michler's ketone and acid halides are: Baither, *ibid.*, 20,1731 (1887), and Staudinger, *ibid.*, 42,3966 (1909).

See Pfeiffer, Goebel and Angern, ***Ann.***, 440, ***265*** (1924), for a reference to colored complexes formed from amino-ketones and some amines.

[6] The following are some selected, recent and pertinent citations: (a) McCay and Schmidt, THIS JOURNAL, 48, 1933 (1926); (b) Nenitzescu, *Bul.* sac. *chim. Romania, 11, 130* (1930); (*Chem. Abstracts,* 24,2458 (1930)).



(A)



(B)

It has been suggested[6b] that the pyrrylmagnesium iodides might be represented in accordance with Formula (B) because they, unlike the related indylmagnesium halides, give a color test. This is an ingenious application of the color test. However, it may be open to the criticism that a compound of Formula (A) might give the color test, not because of the –NMgX grouping (which is known not to give a color test) but because the amine itself (which is liberated from –NMgX compounds by hydrolysis incidental to the completion of the color test) might be the cause of the color. Actually, pyrrole (in the absence of Grignard reagent) does give a blue coloration with iodine and glacial acetic acid, the reagents used to develop the color in testing for reactive organometallic compounds. However, because a more marked color is obtained from a mixture of an RMgX compound and an excess of pyrrole, it appears that the –MgX group is attached to carbon and not to nitrogen. This must not, however, be construed to mean that Formula (B) is necessarily the correct one *prior* to its reactions with a miscellany of compounds. It is entirely possible that no chemical reaction can differentiate between (A) and (B), because the product of reaction gives us no clue as to the original position of the –MgX group. We need only recall a simple illustration: namely, sodium acetoacetic ester which has the sodium attached to oxygen, and yet which (in a reaction with an RX compound) gives a product with the R group attached to carbon and not to oxygen.[7]

Another suggestion for deciding between Formulas (A) and (B) involves the chemiluminescence induced by the oxidation of organomagnesium halides. McCay and Schmidt[8a] observed no luminescence when a small stream of oxygen was played on pyrrylmagnesium iodide. This observation has been confirmed by us in connection with a miscellany of studies on the chemiluminescence of Grignard reagents.[8] We have

[7] This is open to two usual reservations. First, the sodium used need not be attached to oxygen, electronically speaking—in the same way that some would consider no formal valence bond between sodium and chlorine in sodium chloride. Second, some RX compounds react with sodium acetoacetic ester to give an R–O and not an R–C combination.

[8] Gilman, McGlumphy and Fothergill, *Rec. trav. chim.*, 49, 526 (1930). Also Gilman, Fothergill and McGlumphy, *ibid.*, 49, 726 (1930). Other references are to be found in these papers. The *p*-chlorophenylmagnesium bromide was selected because it gives an intense luminescence with oxygen. An answer to the question of the position of the –MgX group in pyrroles and related compounds may be found in absorption spectra studies.

shown that when a known excess of dry and freshly distilled pyrrole is treated with methylmagnesium iodide, phenylmagnesium iodide and p-chlorophenylmagnesium bromide, respectively, and oxygen is then passed into the mixture there is no chemiluminescence. These observations, however, are not to be taken as incontrovertible evidence for the –NMgX linkage, because there is still a possibility that a pyrrole –CMgX linkage may not luminesce

Perhaps the best present way of deciding the position of the –MgX group is by means of the Zerewitinoff reaction. If the –MgX is attached to carbon in accordance with Formula (B), then pyrrole should show at least two active hydrogen atoms inasmuch as another active hydrogen (–NH) is present when the –MgX group in Formula (B) is attached to carbon. If Formula (A) is correct, then but one equivalent of methane should be liberated when pyrrole is treated with an excess of methylmagnesium iodide. Using di-n-butyl ether as a solvent, the number of active hydrogens determined at 29° with freshly distilled pyrrole was 1.049 and 1.045. At a more elevated temperature (heating in a boiling water-bath for one hour) the number was 1.125 and 1.216. These values confirm other related studies.[9] From them one may conclude with definiteness that the –MgX group is attached to nitrogen in accordance with Formula (A), and that in a reaction of the pyrrylmagnesium halide the substituent finds itself generally on the a-carbon atom. This applies to pyrrylmagnesium iodide in di-n-butyl ether under the temperature conditions stated above.

Experimental Part

To those who may be unfamiliar with the carrying out of the color test, it might be stated that it is done very simply by adding a very small volume[2c] of the organometallic mixture to be tested to Michler's ketone in benzene, hydrolyzing with water, and then developing the color with a glacial acetic acid solution of iodine. In the results to be described, no organometallic compound was used. Unless otherwise stated, *a* benzene solution of Michler's ketone was used.

Acetyl Chloride.—Michler's ketone in benzene and acetyl chloride gave a pale blue color which disappeared in one-half minute. The ketone in dimethylaniline with acetyl chloride gave a dark blue color which did not disappear on standing; however, the addition of water destroyed the color. No color was observed when dimethylaniline and acetyl chloride stood for fifteen minutes.

Benzoyl Chloride.—With benzoyl chloride and the ketone a blue color only developed after five minutes. The same mixture with water gives a blue color which reaches maximum intensity in five minutes, and the addition of iodine in glacial acetic acid gives a deeper color, which changes rapidly to brown on the further addition of iodine–glacial acetic acid solution and so would not be confused with the colors given by reactive organometallic compounds.

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[9] Oddo, *Ber.*, 44, **2048** (1911); Ciusa, *Gazz. chim. ital.*, 50, **II**, *53* (1920); *(Chem. Abstracts*, 15, *837* **(1921))**; Fischer and Postowsky, *Z. physiol. Chem.*, 152, *300* **(1926).** See also, Chelintzev and co-workers, *J. Russ. Phys.-Chem. Soc.*, *47*, 1224 (1915); 48, 127 (1916).

Essentially the same color effects were noted when Michler's ketone was replaced by its ethyl homolog, *p,p'*-tetraethyldiaminobenzophenone. Both ketones in dimethylaniline give colors which are destroyed by the iodine solution.

No color was observed after ten minutes, with a mixture of dimethylaniline, benzoyl chloride and water.

Benzoyl Bromide.—Benzoyl bromide appears to have a more pronounced interfering effect than benzoyl chloride.

Furoyl Chloride, C_4H_3OCOCl.—A mixture of the ketone, furoyl chloride and water gave, after ten minutes, a pale green color to the upper layer. This would not be confused with a positive test for an organometallic compound because of the long time required for the development of color subsequent to hydrolysis.

Phosgene, $COCl_2$.—The phosgene solution was that used earlier in a related study.[2e] The colors noted with phosgene may be definitely stated to interfere.

Oxalyl Chloride, $(COCl)_2$.—There is an unmistakable color interference with oxalyl chloride. It is interesting to note that as small a quantity as 0.05 cc. of a 1% solution of oxalyl chloride in benzene gives a pale but distinct blue color with 1 cc. of a 0.01 M solution of Michler's ketone.

Benzene **Sulfochloride,** $C_6H_5SO_2Cl$.—The colors obtained with benzene sulfochloride and Michler's ketone (and *p,p'*-tetraethyldiaminobenzophenone, respectively) should not interfere because they are not the greens and blues obtained with RMgX compounds. Furthermore, even these colors disappear when sufficient iodine–glacial acetic acid solution is added ultimately.

Thionyl Chloride, $SOCl_2$.—A very poor but positive color test is obtained with 1 cc. of a saturated Michler's ketone solution and 0.1 cc. of a 1% thionyl chloride solution in benzene. The color is more pronounced with a larger quantity of thionyl chloride.

Sulfur Chloride, S_2Cl_2.—Neither Michler's ketone nor its ethyl homolog in benzene or dimethylaniline gives a positive or conflicting test with sulfur chloride.

Chloromethyl Sulfate, $ClCH_2OSO_2OCH_3$.—A reddish-purple color is obtained with chloromethyl sulfate.

Phosphorus Pentachloride.—The blue-green color obtained with phosphorus pentachloride definitely interferes in the sense that it would be mistaken for a positive color test with reactive organometallic compounds. This interference was noted with both Michler's ketone and its ethyl homolog.

Pyrrole.—The following facts clarify the observations reported previously.[2f] First, pyrrole and Michler's ketone in benzene give no characteristic color; second, pyrrole and iodine in glacial acetic acid give a blue coloration which might be mistaken for a positive test; third, pyrrole and glacial acetic acid give no characteristic color; and, fourth, an organomagnesium halide (ethylmagnesium chloride or phenylmagnesium bromide) and a definitely known excess of pyrrole with Michler's ketone and glacial acetic acid (without iodine) give what can be regarded as an excellent test.

Miscellaneous.—The following compounds gave no interfering colors: concd. hydrochloric acid, phosphorus trichloride, antimony tri-iodide, anhydrous aluminum chloride, sulfuryl chloride, vanadium oxytrichloride,[10] picryl chloride, di-chloromethyl sulfate $[(ClCH_2)_2SO_4]$, cinnamoyl chloride $[C_6H_5CH{=}CHCOCl]$, tetranitromethane and *p*-toluene sulfochloride.

Summary

A study has been made of the possible interference of some acid halides on the sensitive color test for organometallic compounds. In connection with interfering colors, evidence has been presented for the attachment of

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[10] Kindly provided by Dr. F. E. Brown and F. A. Griffitts.

the –MgX group to nitrogen in pyrrylmagnesium halides. The ultimate disposition of substituents on the α-carbon is accordingly no proof for a –CMgX linkage.

AMES, IOWA

[CONTRIBUTION FROM THE EVANS MEMORIAL AND BOSTON UNIVERSITY SCHOOL OF MEDICINE]

A NEW SERIES OF HALOGENATED SULFONEPHTHALEINS

BY WILLIAM CLOUSER BOYD WITH ALLAN WINTER ROWE

RECEIVED AUGUST 28, 1930 PUBLISHED DECEMBER 18, 1930

Introduction

Sulfonephthaleins with halogen substituted in the phenolic residues have been prepared by several investigators since the initial discovery of the parent body by Remsen.[1] Since certain of the phthaleins and sulfonephthaleins have interesting application as dyes, as indicators, and in certain clinical procedures, a study was begun in 1927 of the preparation of a series of sulfonephthaleins having halogen substituted in the *o*-sulfobenzoic anhydride residue. The selective elimination by the kidney of phenolsulfonephthalein offered a potential lead to direct pyelography if this property were retained in compounds rendered opaque to x-rays by substituted halogen.

In 1929 there appeared a paper by Harden and Drake[2] describing some work on such a series, including four of the compounds described here. They gave but meager details of the preparation, however, and it was felt that the compounds and methods described below might still prove of interest.

Preparation and Properties of the Parent Substances (Tetra-iodo-o-sulfobenzoic Anhydride and Tetrabromo-o-sulfobenzoic Anhydride.—As has evidently been the experience of other workers, it was found that halogen could be not introduced directly into the o-sulfobenzoic anhydride residue of a sulfonephthalein. Attempts to do so resulted in the destruction of the molecule. Consequently the halogen was substituted in the o-sulfobenzoic anhydride molecule before condensation, using a slight modification of the Juvalta method, as described by Pratt and Shupp.[3] Iodine and bromine derivatives were thus prepared with comparative ease. No attempt was made to prepare the fluorine or chlorine derivatives, though the latter could doubtless have been made, as Harden and Drake[2] report the preparation of some of them.

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[1] Remsen, Am. Chem. J., 6, 180 (1884); Lubs and Acree, THIS JOURNAL, 38, 2773 (1916); White and Acree, *ibid.*, 41, 1190 (1919); Orndorff and Sherwood, *ibid.*, 45, 486 (1923); Orndorff and Shapiro, *ibid.*, 46, 2856 (1924).

[2] Harden and Drake, *ibid.*, 51, 562 (1929).

[3] Pratt and Shupp, ibid., 40, 254 (1918).

Tetra-iodo-o-sulfobenzoic Anhydride.—108 g. of o-sulfobenzoic anhydride (Eastman, practical grade) and 300 g. of powdered iodine (4 moles of iodine per 1 mole of anhydride) were mixed in a long-necked flask (an 800-cc. Kjeldahl flask serves very well), and 500 cc. of fuming sulfuric acid containing 50% free SO_3 was added, with stirring. Acid of this strength is ordinarily partly or completely solid. and may require melting. The flask, into the neck of which, to prevent the escape of too much iodine or sulfuric acid, a test-tube was loosely fitted by means of a winding of asbestos cord, was slowly heated in an oil-bath, and the temperature kept between 110 and 120" until the evolution of sulfur dioxide had practically ceased (five to ten hours). The temperature was then raised to 175–180° and held for about thirty minutes. The whole apparatus was then allowed to cool, and when cool the practically solid contents poured into about 1.5 liters of water, and washed with successive portions of water containing sulfurous acid to remove the excess iodine. It was allowed to stand overnight with the final portion of wash water, the solid filtered off, washed with a little water, and dried in air; yield, **333** g. or 88%, calculated on the basis of the amount of o-sulfobenzoic anhydride used. The product so obtained is pure enough for making sulfonephthaleins.

Tetra-iodo-o-sulfobenzoic anhydride is somewhat soluble in water, acetic acid, tetrachloro-ethane, chloroform and benzene. It is quite soluble in acetone and in alcohol, but cannot be recrystallized from either. When dissolved in acetone it forms a dark brown mass, owing, apparently, to the formation of an addition product, since tetra-iodo-o-sulfobenzoic anhydride cannot be recovered from the mass except by the action of some drastic reagent, such as warm nitric acid. In alcohol it supersaturates, forming, when concentrated, a yellow varnish-like mass, which is quite unmanageable. When recrystallized from chloroform it has a melting point of 132" (uncorr.), as against the melting point of the crude product of about 260°, indicating the probable formation of some sort of addition product.

It can, however, be recrystallized from a mixture of alcohol and acetic acid (60 g. will require about 350 cc. of a mixture consisting of 100 cc. of 95% ethyl alcohol and 250 cc. of glacial acetic acid).

The purified product so obtained does not melt, but decomposes at from 305 to 310°. It is somewhat lighter in color than tetra-iodophthalic anhydride, resembling iodoform, except for a slight greenish tinge. The crystals, when examined under the microscope, are seen to be small, imperfect platelets, more opaque than the coffin-shaped crystals of tetra-iodophthalic anhydride.

The compound was analyzed for iodine by the method of Baubigny and Chavanne,[4] other methods, including that of Carius, proving unsatisfactory.

Anal. Calcd. for $C_7O_4I_4S$: I, 74.0; S, 4.6. Found: I, 73.8, 74.1; S, 4.8.

The toxic dose for a rabbit appeared to lie in the vicinity of 0.2 g. per kilogram of body weight when injected intravenously. The substance is not bacteriocidal for B. *coli* except in very high concentrations. One of us (B) took 0.5 g. by mouth without ill effect; subsequently, it could not be demonstrated in the urine.

Tetra-bromo-o-sulfobenzoic Anhydride.—Twenty-five grams of o-sulfobenzoic anhydride, 1 g. of iodine, and 125 cc. of fuming sulfuric acid containing 50% free SO_3 were mixed together in a long-necked flask of about 300 cc. capacity. About **39** cc. (124 *g.)* of bromine was measured out into a flask and added as described below.

About two-thirds of the bromine was added, and the mixture heated to 80° in an oil-bath until the bromine was all absorbed. The apparatus was then allowed to cool to room temperature, when two-thirds of the remaining bromine was added, and the mixture heated to 100° until the bromine was absorbed, as before. The apparatus was again

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[4] Lassar-Cohn, "Organic Laboratory Methods," Oesper–Adams–Clarke, Williams and Wilkins, Baltimore, 1928, p. 443.

allowed to cool, two-thirds of the remaining bromine added, the mixture heated to 130° until absorption of the bromine took place, and again allowed to cool. The next time all of the remaining bromine was added, and the mixture heated to 170° for thirty minutes, and finally allowed to cool. The treatment from this point on is the same as for the iodine derivative; yield, 56 g., or 81%.

The crystals, after washing and drying the crude preparation, have a faint brownish color which deepens on exposure to light, but the pure compound (recrystallized three times from glacial acetic acid) is pure white. The crystals are easily seen under the low power of the microscope to be small, imperfect, hexagonal prisms. After the recrystallized product had been dried in a desiccator over sodium hydroxide to remove traces of acetic acid, the melting point was found to be **219"** (uncorr.).

The neutral equivalent was found to be 258, which corresponds to the calculated molecular weight of 516. The compound was analyzed for bromine by the method of Carius.

Anal. Calcd. for $C_7O_4I_4S$: Br, 61.9. Found: Br, 61.8, 61.8.

The substance is soluble in alcohol, acetone, glacial acetic acid and to some extent in water.

Preparation and Properties of the Halogenated **Sulfonephthaleins.**—For the condensation of the parent substances with phenols, the best condensing agent, both with respect to quantity and to quality of product, was found to be fuming stannic chloride. These anhydrides are much more difficult to condense than the corresponding phthalic anhydride derivatives, and the actual yields were all small.

The decision as to the best condensing agent and also as to optimum temperature was made by treating equal volumes of a standard mixture of melted phenol and anhydride with different reagents at different temperatures, dissolving the product in a slight excess of alkali, diluting to a definite volume, and comparing the resultant colors in the colorimeter.

The preparation of phenol-tetra-iodo-sulfonephthalein may be taken as typical.

Properties of the New Series.—Practically all of these sulfonephthaleins decompose gradually at very high temperatures, but have no real melting points, so as a rule melting points are not given.

PH ranges were determined either by adding a given amount of an alcoholic solution of the substance in question to buffered solutions prepared according to the directions of Folin,[5] or by adding a given amount of 0.04% aqueous solution of the sodium salt of the phthalein. Results obtained by these two methods were identical for the purpose in question.

The buffer mixtures were prepared according to the directions of Clark[6] except that in the PH range 4.6–5.6 the acetic acid mixtures described by Folin[5] were used.

Into these tetra-iodo and tetra-bromosulfonephthaleins more halogen

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[5] Folin, "Laboratory Manual of Biological Chemistry," 4th ed., Appleton and Co., New York, 1925, pp. 49–53.

[6] Clark, "The Determination of Hydrogen Ions," 3d ed., Williams and Wilkins Co., Baltimore, 1928, pp. 192–220.

can be introduced. Bromine can be introduced by boiling the phthalein in acetic acid solution with a slight excess of bromine, pouring into water, extracting with alkali and purifying, as before. Iodine can be introduced, in alkaline solution, by adding a solution of iodine in potassium iodide solution.

Phenol-tetra-iodo-sulfonephthalein.—Eighty grams (0.12 mole) of tetra-iodo-*o*-sulfobenzoic anhydride was dissolved in 320 g. (3.4 moles) of freshly distilled, melted phenol, 80 g. of fuming stannic chloride added, and the mixture heated in an oil-bath for about eight hours. The flask was kept closed by a ground-glass stopper carrying a sealed-in glass tube. Moisture was excluded by a calcium chloride tube.

At the end of about eight hours the mixture was poured into about 6 liters of hot water, and washed repeatedly by decantation and boiling with fresh water. This washed raw product was then extracted with 2% sodium hydroxide solution until only an insoluble residue remained, the extract filtered, and the pbthalein precipitated by the addition of hydrochloric acid. This precipitate was then washed with hot water, as before, and this alternation of solution in alkali, precipitation and washing repeated until the product remained solid in hot water, and was completely soluble in alkali. It was then recrystallized from glacial acetic acid. Harden and Drake report recrystallization from benzene, but this in the experience of the present writers was unsuccessful.

Phenol-tetra-iodo-sulfonephthalein, when pure, consists of small imperfect crystals of a reddish-black color. It decomposes at about 210°. The crystals contain 8 to 10% moisture, which can be driven off by prolonged heating at 180°.

It is readily soluble in methyl alcohol, ethyl alcohol, ethyl acetate, acetone and acetic acid. It is somewhat soluble in benzene, carbon tetrachloride, tetrachloroethane, chloroform and ether. It is only very slightly soluble in water. It dissolves in alkali with an intense purplish color. By dissolving the compound in the calculated amount of alkali and evaporating the solution to dryness, the disodium salt can be obtained, as a dark reddish-black mass, with a bluish tinge. The phthalein dissolves, apparently without permanent change, in concentrated sulfuric acid, with the formation of an intense purplish color. The compound has a useful *P_H* range of 7.0 to 8.2.[7] Its color changes in this interval from a brownish-yellow to a wine-purple.

Phenol-tetra-iodo-sulfonephthalein will dye silk a color which varies from brownish-yellow to reddish-walnut, depending upon the method of application. " Dyeing from a 5% aqueous acetic acid solution is perhaps the simplest laboratory method.

Injected intravenously, as the disodium salt, it is, in part, eliminated through the kidney. It is not toxic to rabbits in doses of 0.2 g. per kilogram of body weight.

Anal. Calcd. for $C_{19}H_{10}O_5I_4S$: I, 59.3. Found: I, 59.0, 58.8, 59.1.

Tetra-iodo-phenol-tetra-iodo-sulfonephthalein.—This compound consists of small, irregular crystals of a reddish-brown color. It is soluble in alcohol, methyl alcohol, ethyl acetate, acetone and acetic acid, but in all to a less extent than is phenol-tetra-iodo-sulfonephthalein. It dissolves in alkali with a green color, and will dye silk a greenish-brown color. It is but slightly soluble in water (the disodium salt) and this renders it unsuited for the ultimate purpose of the study.

The *P_H* range is from 6.2 to 7.0 but as the color simply ranges from one shade of green to another, it is hardly possible that the compound could be of value as an indicator.

Anal. Calcd. for $C_{19}H_6O_5I_8S$: I, 74.6. Found: I, 74.4, 74.2.

Tetra-nitro-phenol-tetra-iodo-sulfonephthalein.—This compound crystallizes in

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[7] Harden and Drake (Ref. *2)* report for the crude product *P*_H 6.4–8.0.

small brown crystals, melting with decomposition at 190°. It dyes silk a peculiar greenish-black. It dissolves in alkali with a purple color. Its *PH* range is probably between 6 and 7, but it is quite unsuited for use as an indicator. It can be analyzed for nitrogen by the Kjeldahl method by first adding zinc dust to the digestion mixture, so as to bring the nitrogen into the reduced form.

Anal. Calcd. for $C_{19}H_6O_{13}I_4N_4S$: N, 5.39. Found: N, 5.20, 5.23.

Diacetyl-phenol-tetra-iodo-sulfonephthalein.—This substance is light brown in color and melts at 136° (uncorr.). It is soluble in the usual organic solvents but practically insoluble in water.

Anal. Calcd. for $C_{23}H_{14}O_7I_4S$: I, 54.0. Found: I, 53.8.

Tetra-bromo-phenol-tetra-iodo-sulfonephthale ($C_{19}H_6O_5Br_4I_4S$).—This substance is brown in color, gives a green color in alkali and dyes silk a greenish-brown color, similar to that given by tetra-iodo-phenol-tetra-iodo-sulfonephthalein, but greener. The disodium salt is practically insoluble in water.

o-Cresol-tetra-iodo-sulfonephthalein.—The properties of this compound are not essentially different from those of phenol-tetra-iodo-sulfonephthalein. It gives a similar purple color in alkali, and dyes silk a shade darker. Its *PH* range was found to be 8.8–9.6.[8] The water solubility is low.

Anal. Calcd. for $C_{21}H_{14}O_5I_4S$: I, 57 4. Pound: I, 57.0, 57.2.

Resorcin-tetra-iodo-sulfonephthalein (**Tetra-iodo-sulfonefluorescein**).—This compound is very difficult to obtain in crystalline form. After washing, on spreading the crystals out to dry, they liquefy to a viscous mass and eventually harden again to a black mass. The solid material is black. It is soluble in the usual solvents. Its solution in alkali is red with a splendid greenish fluorescence. Its *PH* range is about 8 to 10, but it would be quite valueless as an indicator. It dyes silk a golden-reddish-brown.

Anal. Calcd. for $C_{19}H_8O_6I_4S$: I, 58.4. Found: I, 58.4.

Salicylic-acid-tetra-iodo-sulfonephthalein—This compound consists of small, imperfect crystals of a rose-beige color. It is soluble in ethyl alcohol, methyl alcohol, acetone and ethyl acetate. It is not as soluble in acetic acid, chloroform and ether as the compounds previously described. It dyes silk a golden-brown.

Its useful *PH* range is 7.2–8.0, the color changing from yellow-brown to pink. It might prove moderately satisfactory as an indicator.

Anal. Calcd. for $C_{21}H_{10}O_9I_4S$: I, 53.7. Found: I, 53.6.

Phenol-tetra-bromo-sulfonephthalein.—This substance gives very small reddish-black crystals of high but indefinite melting point; its properties are very similar to those of phenol-tetra-iodo-sulfonephthalein. It gives a purple color in alkali, and a golden-yellow on silk. Its PH range was found to be shorter than that of phenol-tetra-iodo-sulfonephthalein, its color changing between *PH* 7.2 and 8.0[9] from a light brown to a purple, so abruptly that its turning point might almost be fixed at *PH* 7.4. It might possibly be of some value as an indicator.

Anal. Calcd. for $C_{19}H_{10}O_5Br_4S$: Br, 47.7. Found: Br, 47.5.

Tetra-bromo-phenol-tetra-bromo-sulfonephthalein.—This substance dissolves in alkali with a bluish-green color, and dyes silk a similar shade, but is not otherwise very different from phenol-tetra-bromo-sulfonephthalein. It is less soluble in the usual solvents.

Its *PH* range was found to be 5.6–7.0,[10] but the colors are a series of shades of bluish-

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[8] Harden and Drake report *PH* 7.0–8.6.

[9] Harden and Drake give *PH* 6.6–8.2.

[10] Harden and Drake report PH 3.0–4.6.

green at all the hydrogen-ion concentrations within this range, so its usefulness as an indicator would probably be small.

Anal. Calcd. for $C_{19}H_6O_5Br_8S$: Br, 64.8. Found: Br, 64.6.

Resorcin-tetra-bromo-sulfonephthalein.—This substance is a black solid, with a greenish sheen. It is soluble in the usual solvents, dissolving in alkali to give a red solution with a magnificent greenish fluorescence. It dyes silk a light reddish-brown. The PH range was difficult to determine, but was about 8–10. The compound would hardly be useful as an indicator.

Anal. Calcd. for $C_{19}H_8O_6Br_4S$: Br, 46.7 Found: Br, 46.5.

o-Cresol-tetra-bromo-sulfonephthalein was also prepared but offered nothing distinctive in its properties.

Tetra-iodo-saccharin.—This compound is not really a member of the present series, but was made while working on the parent substances. It can be prepared by the Juvalta method as described for them.

The substance consists of silky greenish-yellow crystals, somewhat soluble in acetone, and practically insoluble in everything else, including sodium hydroxide solution. It has a faint bitter taste.

The crystals did not melt or otherwise alter even at 345°. They contained carbon, sulfur, iodine and nitrogen, as demonstrated by the usual tests. Analysis for nitrogen was carried out by the Kjeldahl method, a rather long time being required for digestion.

Anal. Calcd. for $C_7HO_3I_4NS$: N, 2.03. Found: N, 1.99.

Attempts to condense this substance with phenolic substances were made, but unlike saccharin itself the substance would not condense.

Summary

Methods of preparing the parent substances of a new series of sulfonephthaleins having halogen substituted in the o-sulfobenzoic anhydride residue are described, together with methods of preparing the phthaleins themselves.

Certain properties of members of the new series, and of another substance, tetra-iodo-saccharin, are given.

BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

THE CUPRO-POTASSIUM CARBONATE SOLUTION IN THE DETERMINATION OF REDUCING SUGARS

BY H. A. SCHUETTE AND JENNETTE N. TERRILL

RECEIVED AUGUST 29, 1930 PUBLISHED DECEMBER 18, 1930

In view of the revival of interest[1] in the use of the so-called cupro-potassium carbonate solution[2] in the determination of reducing sugars, there exists an evident need for more data and for a corroboration of some of those now extant. These ends have in part been approached in this Laboratory by the determination (1) of the dextrose equivalents of four modifications of this solution in which the concentration of copper sulfate is the only variant, and (2) of the levulose equivalent, as affected by change in method of reduction, of still other modifications[3] containing materially less copper than any of the others and, finally, by a study of the action of dextrose upon one of the latter. The presentation of these data is the object of this communication.

Reagents

Six sugar-oxidizing solutions of the type in question were made of such concentrations of copper sulfate, potassium bicarbonate and potassium carbonate as directed by their sponsors. The observed instability[1b,c] of four of these solutions—all statements in the literature to the contrary notwithstanding—made it necessary to prepare them in two parts each of such a concentration of copper sulfate and alkaline salts, respectively, as would produce, when used in the ratio of one volume of the first to four of the second, a reagent of the same composition as that used by its originator. Although a twenty-seven month period of observation on the stability of the fifth member[3] of this group has to date brought out no visible sign of decomposition, yet because of a desire to maintain uniformity in procedure, this reagent also was made up in two parts without, however, disturbing the original proportions of its constituents. The compositions of the copper solutions which were used throughout this study are given in Table I.

In the preparation of solutions "B" of the above reagents (Ost's and Nyns' modifications) the normal carbonate was slowly added to about 700 cc. of water at, or near, its boiling point. Complete solution of this salt was then effected by the addition of the acid carbonate. The same tech-

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[1] Nyns, *Sucrerie Belge*, 44, 210 (1924); *Bull. assoc. école sup. brasserie Louvain*, *25*, 63 (1925); (a) Jackson, *J. Assocn. Official Agr. Chem.*, *9*, 178 (1926); (b) Jackson, *ibid.*, 12, 166 (1929); (c) Schuette and Terrill, *ibid*, **13**, 93 (1930); (d) Zerban and Sattler, *Ind. Eng. Chem., Anal. Ed.*, 2, 307 (1930).

[2] For a bibliography of this solution see *J. Assocn. Official Agr. Chem*, *13*, 97–98 (1930).

[3] Beyersdorfer, *Z. Ver. deut Zuckerind.*, *69*, 403 (1919).

TABLE I

COMPOSITION OF CUPRO-POTASSIUM CARBONATE SOLUTIONS

Sponsor	Solution A $CuSO_4 \cdot 5H_2O$, g. per liter	Solution B K_2CO_3	 $KHCO_3$ g. per liter
Ost[4]	117.8	312 5	125
Ost[5]	87.5	312 5	125
Reyersdorfer[3]	15.71	312.5	125
Beyersdorfer[3]	3.14	312.5	12.5
Nyns[1]	75.0	312.5	125
Nyns[1]	126.5	312 5	125

nique was followed in making the Beyersdorfer modifications except that the water was brought to a temperature of only 60° before the carbonates were added in the same manner and order.

The dextrose used in this study was obtained from the Bureau of Standards (standard sample 41), and the levulose from the Eastman Kodak Company. The latter was found to have the same copper equivalent as a sample obtained from the former source.

Experimental Procedure

Exactly 20 cc. of the reducing solution, containing varying amounts of sugar, was added to 50 cc. of the freshly mixkd cupro-potassium carbonate reagent combined in the proportion of 10 cc. of solution A and 40 cc. of solution B. The dextrose–copper equivalents were determined for the two solutions of Ost[4,5] and the two of Nyns[1] by the procedure described elsewhere.[1c,d] Reductions were carried out for two and one-half hours at a temperature of 48.9 ± 0.1°, in stoppered Erlenmeyer flasks immersed to within 3 cm. of the top. The precipitated cuprous oxide was determined gravimetrically. Duplicate determinations run side by side checked excellently.

The levulose–copper equivalents of Beyersdorfer's stronger solution[3] were determined by three methods of reduction in which time and temperature were the variants, the approximate relationship between these factors being an inverse one. The conditions were met by following the *modus operandi* of Munson and Walker,[6] Defren[7] and Nyns,[1] respectively, for effecting the reduction of the copper solution. The phenomenon of delayed flocculation'' of part of the cuprous oxide was not detectable in this series of reductions.

Inasmuch as the graph of the observed reducing sugar–copper equivalents of the oxidizing solutions proved to be a straight line, there was derived for each a mathematical expression for the dual purpose of dis-

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[4] Ost, *Ber.*, 23, 1035 (1890).

[5] Ost, *Chem.-Ztg.*, 19, 1784 (1895).

[6] Munson and Walker, THIS JOURNAL, 28, 663 (1906).

[7] Defren, *ibid.*, 18, 749 (1896).

tributing the experimental errors over the whole range and of calculating the sugar equivalents for any weight of copper. It is in this form that the data obtained in this investigation are recorded (Tables II and III).

TABLE II

THE DEXTROSE EQUIVALENT OF THE CUPRO-POTASSIUM CARBONATE SOLUTION

Copper content, mg per cc.	Range of concn. of dextrose (x) in 20 cc., mg.	Equation for calculating Cu equiv.	Mean deviation $Cu_{obs.} - Cu_{calcd.}$, mg.
19.1'	60–140	$0.2254x - 4.3725$	±0.21
22.3[5]	60–140	$.2276x - 5.2175$	± .14
27.9[4]	60–140	$.2220x - 2.5700$	± .47
39.3[1]	20–140	$.2198x - 0.6650$	± .50

x = mg. of dextrose; y = mg. of copper.

TABLE III

THE LEVULOSE EQUIVALENT OF THE CUPRO-POTASSIUM CARBONATE SOLUTION (BEYERSDORFER)

Method	Time of reduction, min.	Equation for calculating levulose equiv. (x) from Cu	Mean deviation $Cu_{obs} - Cu_{calcd.}$, mg.
Over a free flame[6]	6	$2.485x - 2.255$	±0.20
In a boiling water-bath'	15	$2.391x - 1.034$	± .43
In a water-bath at 48.9°[1]	120	2.549~ – 1.464	± 51

The assertion by Nyns,[1] now known to be erroneous,[1b,c] that the cupro-potassium carbonate solution under closely guarded conditions as to time, temperature and concentration is a selective reagent for levulose to the exclusion of dextrose, suggested the desirability of observing what action, if any, the latter has upon Beyersdorfer's alternative modification[3] of this oxidizing agent which contains but one-fifth as much copper. To that end a series of dextrose solutions (**0.3** g. in **100** cc.) of **20** cc. each was added to 50-cc. portions of the copper solution which had been mixed as above described and then brought to the reaction temperature (48.9'). The amount of copper reduced was determined at one-half hour intervals until a reaction time of two and one-half hours was reached. Data are presented in the form of a graph (Fig. **1**).

Discussion

The maximum quantity of dextrose which any of the four reagents relevant to this study will oxidize is of the order of magnitude of **140** mg. On comparing the several dextrose–copper equivalents as calculated by means of the corresponding equation (Table II) it will be noted that there exists an exception to the generalization that the oxidizing power of the cupro-potassium carbonate reagent rises with an increase in the concentration of the copper. The situation which obtains is that the Ost solution[6] in which there are 22.3 mg. of copper per cc. will oxidize less dextrose than that one of Nyns[1] in which the concentration is less, or 19.1 mg. Inasmuch as the equilibrium conditions within this reagent are apparently not much better understood now than at the time of its introduction by Soldaini,[8] no explanation of this phenomenon suggests itself except that it is perhaps its hydrogen-ion concentration which is the significant factor.

The application of the Ost solutions to the determination of dextrose under the unified conditions of this study is new for data obtained by their sponsor were based on a larger volume of reactants (150 cc.) when boiled for at least ten minutes. In view of the data communicated herein it appears that, as between these two reagents for the determination of dextrose under the conditions proposed by Nyns,[1] preference should be given the weaker solution[6] because of its greater sensitiveness and the fact that the mean deviation between observed and calculated weights of reduced copper was materially less for this modification.

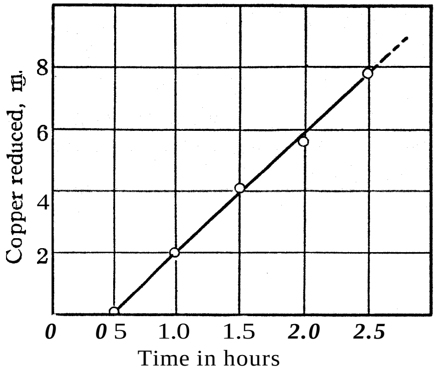

Fig. 1.—Action of dextrose upon Beyersdorfer's cupro-potassium carbonate reagent.

No claim had ever been advanced by its sponsor that the weakest copper solution[3] which has been used in this study is quite indifferent in the presence of dextrose. Beyersdorfer, it is true, carried out his reductions in a short time, compensating for brevity of reaction by recourse to higher temperatures. The rather high ratio of the relative reducing effects of dextrose and levulose upon Nyns' stronger solution—10 mg. of copper was found to be equivalent to 3.5 mg. of levulose'' or 48.5 mg. of dextrose[9]—raised the hope that, by applying his conditions to a reagent of still lower copper content, it might be demonstrated that it shows a selective reactivity for the latter sugar and therefore could be developed as a serviceable tool in the determination of this ketose in the presence of dextrose, a situation which obtains in the analysis of honey. This hope was not realized (Fig. 1). No reduction which is measurable by macro-chemical means had taken place at the end of the first half-hour of the reaction period, but after that it progressed arithmetically.

It is not improbable, however, that with the establishment of the above-mentioned ratio with respect to this reagent it will be possible to calculate

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[8] Soldaini, *Pubb. Instit. studi Sup. Firenzi Sez. med. chir.*, **1**, 232 (1876); *Gazz. chim. ital.*, **6**, 322 (1876).

[9] This ratio is in good agreement with that reported by Jackson[1b] who found that 13 mg. of dextrose precipitate the same weight of copper as 1 mg. of levulose.

the percentage of these two sugars in a mixture, although such a procedure bids fair to be a laborious task, one that will involve many approximations.

Beyersdorfer's stronger reagent has not heretofore been put to a comparative test as to its levulose oxidizing powers when time and temperature of reaction are made to vary. As a result of such a study it appears (Table III) that no very material differences exist in the levulose–copper equivalents as between a reaction period of six minutes at the temperature obtainable by interposing an asbestos gauze between a beaker and a Bunsen burner,[6] by extending that period to fifteen minutes and reducing the temperature to that of a boiling water-bath,' or by allowing the reduction to proceed slowly.[1] The levulose equivalents of 10 mg. of copper are, under the above conditions and in the order given, 4.9, 4.6 and 4.5, respectively.

Choice of method of reduction will therefore be determined to some extent by (1) the smallest mean deviation between observed and calculated values, (2) convenience of operation, **(3)** reproducibility of results and (4) probable popularity among analysts. The mode of reduction of Munson and Walker[e] fulfils these requirements.

Summary

In a re-investigation of the so-called cupro-potassium carbonate solution of Soldaini[8] as modified in turn by Ost[4,5] and by Nyns,[1] there have been obtained data on the dextrose equivalents of four forms of this reagent of a copper content lying between the limits of 19.1 and **39.3** mg. per cc. These data are presented in the form of mathematical expressions and are pertinent to a temperature of 48.9° maintained for two and one-half hours. It was also found that this sugar, under the aforesaid conditions, has a reducing action upon that modification by Beyersdorfer[3] which contains but 0.8 mg. of copper per cc. This observation casts some doubt upon the acceptance of this solution as a selective reagent for levulose when both are present in the same solution.

Mathematical expressions also have been derived for calculating the levulose–copper equivalents of another reagent of this type (copper content 4.03 mg. per cc.) when either one of three modes of reduction is used, the relevant variants being time and temperature so adjusted as to bear to each other a relationship which is approximately an inverse one. It has been pointed out that there exist no very material differences in the levulose equivalents of a given weight of cuprous oxide when the latter is precipitated by either one of these procedures.

MADISON. WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND]

SOME GAMMA-NITRO-BETA-FURYLBUTYROPHENONES[1]

BY NATHAN L. DRAKE AND H. W. GILBERT

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The addition of nitromethane and phenylnitromethane to α,β-unsaturated ketones such as benzalacetophenone has been studied extensively by Kohler and his pupils.[2] The work herein described is concerned with the preparation of certain γ-nitro-β-furylbutyrophenones, prepared by means of the addition of nitromethane and phenylnitromethane to furfuralacetophenone and furfural *p*-bromo-acetophenone.

Furfuralacetophenone has been prepared by Kostanecki and Podrajansky[3] and by Semmler and Ascher[4] but in each investigation the substance was obtained as an oil which apparently was not obtained in crystalline form. After considerable difficulty our oily product, prepared by condensation of furfural and acetophenone by means of 10% sodium hydroxide, was induced to crystallize. It formed long blunt yellow crystals which turned red on standing, and darkened rapidly in the sunlight. No difficulty was encountered in obtaining crystalline furfural-*p*-bromo-acetophenone. The latter substance also darkens on standing, but is much more stable than furfuralacetophenone.

The addition of nitromethane to the above-mentioned unsaturated ketones was carried out in a manner similar to that used in the case of benzalacetophenone. The furfural derivatives, however, are much more soluble in the reaction mixture than are the benzal derivatives, and consequently must be precipitated at the completion of the reaction by the addition of water. The use of a large excess of nitromethane was found necessary to give the best yields. Both products are very soluble in methyl and ethyl alcohols, ether and acetone, but sparingly soluble in petroleum ether.

The addition products of phenylnitromethane crystallize readily and were prepared with far less difficulty than the corresponding nitromethane addition products.

Experimental

Furfuralacetophenone.—A solution of 22 g. of stick sodium hydroxide in 196 cc. of water and 100 cc. of 95% ethyl alcohol were introduced into a beaker loosely covered

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[1] From a thesis submitted to the Graduate School of the University of Maryland by H. W. Gilbert in partial fulfilment of the requirements for the degree of Master of Science.

[2] Kohler and co-workers, THIS JOURNAL, 38, 889 (1916); 41, 1644, 1697 (1919); 44, 624 (1922); 45, 2144 (1923); 50, 884 (1928).

[3] Kostanecki and Podrajansky, *Ber.*, 29, 2248 (1896).

[4] Semmler and Ascher, *ibid.*, 42, 2356 (1909).

with a disk of cardboard and provided with an efficient mechanical stirrer. Into the alkaline alcoholic solution was poured **52 g.** of acetophenone, the stirrer was started and **42** g. of freshly distilled furfural was added slowly. Considerable heat was evolved at first and ice cooling was necessary to prevent the temperature from rising too high. After ten minutes the ice was replaced by water and the water-bath kept at 20–30° for three hours to complete the condensation. The water was then replaced by an ice and salt mixture, and after the temperature of the reaction mixture had become constant, a seed of furfuralacetophenone was added. Stirring was continued during the separation of the yellow granular condensation product. One-half hour was sufficient for crystallization. The crude product was sucked as dry as possible on a *cold* Büchner funnel and then dissolved in chloroform. After having been dried over sodium sulfate the chloroform was distilled off and the residue distilled *in vacuo*. Eighty grams of product was obtained. Furfuralacetophenone melts at 26°, and boils at 179° at **7** mm. pressure. Under **764** mm. pressure, the substance distils with considerable decomposition at 319°.

Furfural-*p*-bromo-acetophenone.—This substance was prepared as described above for furfuralacetophenone The crude material boiled at 210–217° under **16–18** mm. pressure and melted at **79–80°**. Recrystallization from hot ethyl alcohol yielded a product melting at 80–81°.

Anal. Calcd. for $C_{13}H_9O_2Br$: C, **56.3**; **H, 3.25.** Found: C, **56.2,** 56.2; H, 3.6, 3.5.

γ-Nitro-β-furylbutyrophenone.—To **35** g. of furfuralacetophenone in **50** cc. of dry methanol in a covered beaker provided with an efficient mechanical stirrer and heated in a beaker of boiling water was added rapidly a suspension of sodium nitromethane prepared by the addition of **40 g.** of nitromethane to a well-cooled solution of **11** g. of sodium in **175** cc. of dry methanol. The container from which the suspension was added was rinsed with **100** cc. of dry methanol and the rinsings added to the reaction mixture. The latter was kept hot and stirred to insure the rapid course of the addition, which was marked by the disappearance of the solid. When all of the sodium nitromethane had disappeared, the mixture was cooled *immediately* in an ice and salt bath and acidified *very slowly* (over about forty-five minutes) with **60** cc. of glacial acetic acid. Stirring was continued for thirty minutes longer, the solution was then seeded with a crystal of the addition product and **150** cc. of water was added slowly to precipitate the nitro ketone. After thirty minutes the solid was filtered off, washed on the funnel with **500** cc. of water and three ***50-cc.*** portions of 75% ethyl alcohol; **40** g. of a crude product, melting at 48°, was obtained. This was purified by dissolving it in the minimum quantity of 95% ethyl alcohol, adding **3** g. of norite and stirring the mixture for five hours. The charcoal was then filtered off and the product caused to crystallize by adding water. Thirty-five grams of material melting at 49.5–50° was obtained in this way.

Anal. Calcd. for $C_{14}H_{13}O_4N$: C, **64.85;** H, **5.02.** Found: C, **65.0, 64.9;** H, **5.17, 5.20.**

γ-Nitro-β-furyl-*p*-bromobutyrophenone.—This substance was prepared by the method described above for γ-nitro-β-furylbutyrophenone. For purification a charcoal treatment of a solution of the ketone in a mixture of one part acetone to nine parts of ethyl alcohol was used. The yield of purified material corresponded to **75%** of that theoretically possible. The product melted from **72** to 73°.

Anal. Calcd. for $C_{14}H_{12}O_4NBr$: C, **49.7;** H, **3.55.** Found: *C*, 49.9, 49.8; H, **3.84, 3.78.**

γ-Phenyl-γ-nitro-β-furylbutyrophenone.—19.8 grams of furfuralacetophenone was dissolved in **100** cc. of dry methanol in a round-bottomed flask fitted with a reflux condenser. To the solution was added **13.7** g. of phenylnitromethane dried over phosphorus pentoxide. The mixture was made alkaline by adding a solution of 0.5 ***g.*** of sodium in **10** cc. of dry methanol, then refluxed for three hours, and cooled in an ice and salt mixture with occasional shaking. The product which crystallized was sucked as dry as possible on a funnel and washed with **25** cc. of 95% ethyl alcohol which had been cooled on an ice and salt bath; **25** g. of a product melting from **90** to 105° was obtained. Recrystallization from alcohol yielded 18 g. of nitro ketone, melting at **153** to **153.5°**.

Anal. Calcd. for $C_{20}H_{17}O_4N$: C, **71.7**; H, **5.07**. Found: C, **71.7, 71.8**; H, **5.11, 5.20.**

γ-Phenyl-γ-nitro-β-furyl-*p*-bromobutyrophenone.—This ketone was prepared as described for γ-phenyl-γ-nitro-β-furylbutyrophenone. **A 29%** yield of product melting at **87** to 88.5° was obtained.

Anal. Calcd. for $C_{20}H_{16}O_4NBr$: C, **58.0**; H, **3.86**. Found: **C, 57.8, 57.8; H, 3.81, 3.75.**

Summary

The addition products of nitromethane and phenylnitromethane to furfuralacetophenone and furfural-*p*-bromo-acetophenone are described.

College Park, Maryland

[Contribution from the Chemistry Laboratory of the University of Michigan]

THE REACTION BETWEEN THE BINARY SYSTEM MAGNESIUM + MAGNESIUM IODIDE AND AROMATIC ALDEHYDES

By M. Gomberg and W. E. Bachmann

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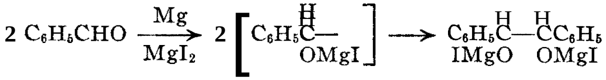
From the behavior of ketones, benzils and acids toward a mixture of magnesium and magnesium halide[1] it was inferred that the carbonyl group in aldehydes as well would be affected in a similar manner. Thus, benzaldehyde, the aldehyde which we have studied most in detail, should react as follows



$$2\,C_6H_5CHO \xrightarrow[MgI_2]{Mg} 2\left[\begin{matrix}C_6H_5\overset{H}{C}— \\ \quad OMgI\end{matrix}\right] \longrightarrow \begin{matrix}C_6H_5\overset{H}{C}—\overset{H}{C}C_6H_5 \\ IMgO\quad OMgI\end{matrix} \qquad (1)$$

I

It was found that the binary system reacts with benzaldehyde. Although, in reality, no hydrobenzoin to correspond to compound (I) is obtainable on the hydrolysis of the reaction mixture, there is nonetheless every reason to assume that the reaction indicated actually represents the first stage of the process. The disappearance of this intermediate product (I) is brought about by reactions subsequent to that given as the first step (Equation 1). We found, namely, that this hydrobenzoinate salt, which readily can be prepared directly from hydrobenzoin itself by treatment with methylmagnesium iodide, rapidly and completely reduces benzaldehyde to iodomagnesium benzylate (111), and thus becomes oxidized to iodomagnesium benzoate (II).

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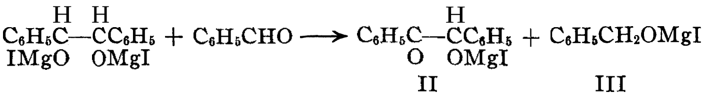
[1] Gomberg and Bachmann, This Journal, 49, 236 (1927); 49, **2584 (1927); 50,2762 (1928);** Gomberg and Bailar, *ibid.*, **51,2229 (1929);** Gomberg and Van Natta, *ibid.*, **51,2238 (1929);** Bachmann and Shankland, *ibid.*, 51,306 **(1929).**

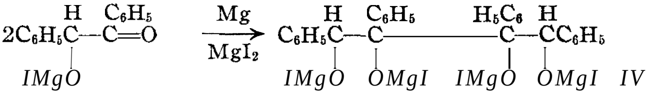


$$C_6H_5\underset{\text{IMgO}}{\overset{\text{H}}{C}}-\underset{\text{OMgI}}{\overset{\text{H}}{C}}C_6H_5 + C_6H_5CHO \longrightarrow \underset{\text{II}}{C_6H_5\underset{\text{O}}{C}-\underset{\text{OMgI}}{\overset{\text{H}}{C}}C_6H_5} + \underset{\text{III}}{C_6H_5CH_2OMgI} \qquad (2)$$

The speed of Reaction 2 is ever so much greater than that of 1, so that in the reaction between benzaldehyde and the binary system no appreciable amount of hydrobenzoinate can remain present as such. As soon as formed it becomes oxidized by the portion of the aldehyde which is still unchanged.

However, when the reactants are taken in the proportion indicated jointly by Equations 1 and 2 (*i. e.*, 3 moles of aldehyde + 1 atom of magnesium), then the final reaction mixture, hydrolyzed, still contains invariably some unchanged aldehyde; the amount of benzoin is only about half of that calculated, and there is present, in addition, nearly an equal amount of a resinous substance of approximately the same composition as benzoin but of a much higher molecular weight than the latter. On the other hand, when, instead of one atom, an excess of metallic magnesium is taken, the total consumption becomes finally 1.5 atoms of the metal for 3 molecules of the aldehyde, and no more than that even when the reaction period is allowed to extend for two years. The reaction mixture yields now the calculated amount (1 mole) of benzyl alcohol, but no benzoin, while the polymerized resin is proportionately larger in amount. Obviously the resinous substance must be continually being formed at the expense of the benzoinate salt (II) through a third step in the process, which step is brought about, like the first step, again by the binary system.

Indeed, the benzoinate salt, as a ketone, should be susceptible to reduction



$$2C_6H_5\underset{\text{IMgO}}{\overset{\text{H}}{C}}-\overset{C_6H_5}{C}{=}O \xrightarrow[\text{MgI}_2]{\text{Mg}} C_6H_5\underset{\text{IMgO}}{\overset{\text{H}}{C}}-\underset{\text{OMgI}}{\overset{C_6H_5}{C}}-\!\!-\!\!-\underset{\text{IMgO}}{\overset{H_5C_6}{C}}-\underset{\text{OMgI}}{\overset{\text{H}}{C}}C_6H_5 \quad \text{IV} \qquad (3)$$

That salt, prepared directly from benzoin itself by the use of just enough methylmagnesium iodide to affect only the hydroxyl group, was found to react, although somewhat slowly, with the binary system. While the amount of metallic magnesium consumed corresponds near enough to that required by Equation 3, the quantity of tetraphenylerythritol produced is only 5 to 12% of the calculated, the rest consisting of polymerized resin which, however, appears to be identical with that obtainable when one starts with benzaldehyde itself,

The conclusion, therefore, seems justified that the mechanism of the reaction between the binary system and benzaldehyde consists in three consecutive steps, and these commence to overlap each other soon after the reaction ensues: (1) reduction by the binary system, in moderate speed, of the aldehyde to hydrobenzoin salt; (2) very rapid oxidation of the salt produced by still unchanged aldehyde to the salt of benzoin;

(3) slow reduction of the latter again by the binary system, with simultaneous, or subsequent, polymerization or condensation. The relative proportions of benzoin and polymer will depend in each case upon the comparative speeds of Reactions 1 and 3, respectively, and upon how nearly the amount of magnesium consumed approaches the ratio of 1.5 atoms for 3 moles of aldehyde.

It still remains to determine the constitution of the polymer and the factors which induce its fortnation from the tetraphenylerythritol salt (IV). Nor can we offer at this time any explanation why, when starting with pure iodomagnesium benzoinate, one gets on reduction with MgI, in addition to the resin, at least 5–10% of tetraphenylerythritol, while when starting with benzaldehyde, the final reduction product consists wholly of the polymerized resin. Other aromatic aldehydes that have been investigated in this Laboratory by Mr. R. V. Shankland were found to react with the binary system essentially in the same manner as benzaldehyde.

The fact that the binary system—with the surmised MgI as the real active reducing agent—is generally very analogous in its effects to that of metallic sodium, suggests that the mechanism of the much discussed reaction between sodium and aldehydes is fundamentally similar to that between our binary system and aldehydes.

Experimental

Numerous experiments were carried out, varying the relative amounts of the principal reactants, using small amounts and large amounts of magnesium iodide, and allowing the reaction to run for periods from a few hours to two years. Only a few experiments, typical of the others, are here described.

It was established that benzaldehyde and magnesium iodide, in the absence of metallic magnesium, form merely a molecular complex, which, in the form of an etherate, separates as a heavy oil insoluble in the ether–benzene mixture employed as a solvent. On hydrolysis the complex is resolved completely into its components. With magnesium bromide, a crystalline complex is formed which, by coating the metallic magnesium, greatly slows down the reaction although in the end the same reduction product is formed. For this reason, magnesium iodide is to be preferred.

Benzaldehyde (3 Moles) + **Mg** (1 Atom) + **MgI_2.**—To a filtered solution of magnesium iodide, prepared from 70 g. of iodine and excess magnesium powder, in a mixture of 125 cc. of absolute ether and 150 cc. of dry benzene, were added 53 g. of benzaldehyde and 4.1 g. of magnesium ribbon. The jar was tightly closed with a stopper and placed on a shaking machine. After several days the insoluble oil, the complex of benzaldehyde and magnesium iodide, nearly all disappeared, and by the end of two weeks all the magnesium had dissolved. The solution, hydrolyzed with dilute acid and additian of more benzene, was extracted with a solution of sodium carbonate (yield of benzoic acid, 12 g) and the solvents, ether and benzene, were removed by distillation under reduced pressure. The residue was digested with ether, the precipitated benzoin. only slightly soluble in ether, was removed by filtration; to the filtrate was added some petroleum ether, which induced separation of more benzoin. In all, 15.1 g. of benzoin was obtained. Distillation of the filtrate under a pressure of 1 mm. on a steam-bath gave 15 g. of an oil, from which, by use of sodium bisulfite, there were obtained 3 g. of benzaldehyde and 11 g. of benzyl alcohol. The non-volatile portion of the reaction mixture, the polymerized resin, weighed 15 g.

In another experiment, with only 3.6 g. of metallic magnesium, the reaction was finished after the mixture was heated on a steam-bath for twelve hours. The result was 17.5 g. of benzoin, 4 g. of unchanged aldehyde, 10 g. of benzyl alcohol and 15 g. of resin.

In experiments in which only small amounts of magnesium and magnesium iodide were employed, considerable quantities of benzyl benzoate were formed. The condensation of the aldehyde to the ester is here brought about in virtue of the catalytic influence of iodomagnesium benzylate, an effect similar to that of sodium benzylate.

Benzaldehyde (3 Moles) + Mg (1.5 Atom) + MgI_2.—Benzaldehyde, 106 g., was added to a solution of 150 g. of magnesium iodide in a mixture of 200 cc. of ether and 300 cc. of benzene. Magnesium turnings, 12.2 g., were introduced and the mixture, protected from access of air by a mercury trap, was boiled under a reflux condenser. After twenty hours of heating, the magnesium was nearly all gone. The mixture was hyrolyzed, the mixed solvents removed by distillation and replaced by ether alone, but no precipitation of benzoin occurred. The ether was then evaporated, the benzyl alcohol distilled under 1 mm. pressure and the non-volatile material extracted repeatedly with petroleum ether. There were isolated: benzaldehyde, none; benzoin, 2.5 g.; benzil, 1 g.; benzyl alcohol, 30 g.; resin, 65 g.

In another experiment, with the reactants in the same amounts as above and the magnesium in long ribbon strips, the mixture was placed in a one-liter graduated cylinder and the reaction allowed to proceed at room temperature. The magnesium was all dissolved in ten weeks. No benzaldehyde was left and no benzoin obtained, the reaction products consisting solely of benzyl alcohol and the resin.

Benzaldehyde + Mg (Excess) + MgI_2.—A mixture, in ether–benzene, of 53 g. of benzaldehyde, 75 g. of magnesium iodide and 8 g. of metallic magnesium was boiled for thirty hours. However, the amount of magnesium that reacted was only 6.35 g., i. e., 1.5 atoms for 3 moles of the aldehyde, and the reaction products were benzyl alcohol, 15.2 g., and polymerized resin.

In a series of experiments, with 53 g. of aldehyde in each and with large excess of magnesium in form of strips, the reaction was allowed to proceed at room temperature from a year to eighteen months, but the loss in weight of magnesium was again about the same, namely, 6.36, 6.7, 6.36, 6.77 g., respectively. In still another experiment, the mixture was allowed to stand for two years—the loss in weight of the metal was 6.42 g., and the magnesium hydroxide produced on hydrolysis of the reaction mixture required 135 cc. of 4 N acid instead of the calcd. 132 cc. The products were benzyl alcohol and resin.

Oxidation of Iodomagnesium Hydrobenzoinate by Benzaldehyde to Iodomagnesium Benzoinate (Equation 2).—While hydrobenzoin itself is without effect upon benzaldehyde, the salt readily reduces it to benzyl alcohol. The salt was prepared by adding solid hydrobenzoin to a solution of methylmagnesium iodide until evolution of methane no longer took place.

$$C_6H_5CH(OH)CH(OH)C_6H_5 + 2CH_3MgI = C_6H_5CH(OMgI)(IMgO)CHC_6H_5 + 2CH_4$$

To such a solution, prepared from 10.6 g. of hydrobenzoin, 5.3 g. of benzaldehyde was added. The reaction was complete after the mixture had been warmed for five to ten minutes. From the mixture, hydrolyzed, there was isolated 9.5 g. of benzoin and 3 g.

of benzyl alcohol. In many experiments on a larger scale the yields also of alcohol obtained were much nearer to those calculated.

The reduction of benzaldehyde by the hydrobenzoinate salt consists in the transfer of an H and MgI from the salt to the aldehyde. That only one of the two groups (HCOMgI) is involved in this transfer has been proved in several ways, (a) Were the second group also involved, the reaction would then become as follows

$$C_6H_5COCH(OMgI)C_6H_5 + C_6H_5CHO = C_6H_5COCOC_6H_5 + C_6H_5CH_2OMgI \quad (4)$$

In reality, however, the reverse of this occurs—iodomagnesium benzylate reduced benzil to the benzoinate salt, itself becoming oxidized to aldehyde. In an experiment with iodomagnesium benzylate from 8 g. of alcohol with 8 g. of benzil, there was isolated 4.6 g. of benzoin and 1.9 g. of benzaldehyde. (b) Whether we start with benzaldehyde and the binary system, or with the aldehyde and the hydrobenzoinate salt, the actual presence of iodomagnesium benzoinate as one of the main resulting products has been confirmed by subjecting the mixture of the reaction products, prior to hydrolysis, to the action of phenylmagnesium iodide. In each case, then, after hydrolysis, triphenylethylene glycol resulted.

$$C_6H_5COCH(OMgI)C_6H_5 + C_6H_5MgI = (C_6H_5)_2C(OMgI)CH(OMgI)C_6H_5 \quad (5)$$

In one experiment, using 21 g. of benzaldehyde, 5.2 g. of pure triphenylethylene glycol was obtained, m. p. 168°. In another experiment, starting with 2.4 g. of hydrobenzoin, 2.5 g. of the same glycol was isolated from the mixture of the reaction products.

Reduction of Iodomagnesium Benzoinate by Mg + MgI_2.—To a solution of 20 g. of benzoin and 16.5 g. of magnesium iodide in a mixture of 30 cc. of ether and 80 cc. of benzene, a concentrated ether solution of ethylmagnesium iodide was gradually added until no more ethane was being evolved. Magnesium powder, 2.5 g., was now added and the mixture refluxed on a steam-bath for fifteen hours. The solution was filtered and decomposed with dilute acid. Fine threads of tetraphenylerythritol crystallized from the solution, and some more from the filtrate, 2.8 g. in all, which is 14% of that possible. The remaining 17 g. of product consisted of the polymerized resin. Other similar experiments varied in yield of tetraphenylerythritol from 3 to 20% of the calculated. The erythritol compound melted at 236°, and is identical with that which Kaufmann[2] obtained by electrolytic reduction of benzoin. By oxidation with copper sulfate in pyridine it gives benzil, almost weight for weight.

The Resinous Component of the Reaction Mixture.—This material, whether obtained in the process of reduction by means of the binary system either of benzaldehyde or of iodomagnesium benzoinate, has the consistency of a thick sirup if the removal of the benzyl alcohol has been done merely by distillation under reduced pressure. The last traces of alcohol are best removed by steam distillation. If the resinous mass is now dissolved in ether and, after thorough drying of the solution, is completely freed from the solvent, it is obtained as a yellow, transparent, solid, brittle mass of the appearance of rosin. It softens at about 50° and is all molten at about 60–65°. It is insoluble in petroleum ether. It remains entirely dissolved in ethyl ether when the solution is fairly concentrated—about 1 to 5—but on further dilution there separates, about 10% by weight, an amorphous white powder which is only very slightly soluble in ether and which melts at 160 to 180°. The original resinous mass is probably a mixture of several individual substances. It has an average molecular weight of 600 to 800 and a percentage composition of carbon and hydrogen not far from that of tetraphenylerythritol itself. Treatment with acids or alkalies, or acetylation, gave unsatisfactory results. While the erythritol (m. p. 236°) gives on oxidation with copper sulfate in pyridine benzil almost quantitatively, the resin is unaffected by that reagent, which makes it appear hardly probable that the resin contains stereoisomers of this crystalline erythritol.

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[2] Kaufmann, *Z. Elektrochem.*, 4, 461 (1898).

Various Aromatic Aldehydes and the System **$MgI_2 + Mg$.**[3]—Other aromatic aldehydes were found to react with the binary system essentially in the same manner as benzaldehyde. When excess of magnesium was employed and the reaction was allowed to go to completion, just slightly more than 0.5 gram atom of magnesium dissolved for each mole of aldehyde reduced. Under those circumstances no corresponding benzoin was obtained, the only products being the primary alcohol and viscous oil analogous to the resin resulting from benzaldehyde. If, however, the reduction was only allowed to proceed until the complex of the aldehyde with magnesium iodide had disappeared, during which time approximately two-thirds of the maximum amount of metallic magnesium had dissolved, or when only that limited amount of magnesium was used for the reaction, then a fair yield of the corresponding benzoin resulted. These substituted benzoins, unfortunately, proved, in general, so soluble that they could not be separated readily from the viscous condensation products which always accompanied the other products. It was found advantageous to treat the mixture of the benzoin and the viscous oil with a solution of cupric sulfate in pyridine, thus obtaining the corresponding benzils. These proved usually only sparingly soluble in benzene or acetic acid and could, therefore, be more readily separated. The results are summarized in Table I. Excess of magnesium iodide was used in each case, while the amount of magnesium was one-third of an atom to a molecule of the aldehyde. The solvents used for each experiment comprised 75 cc. of ether and 150 cc. of benzene.

TABLE I

REDUCTION OF ALDEHYDES BY BINARY SYSTEM

Aldehyde reduced	Moles	G.	Alcohol obtained	G.	Benzoin isolated as	G.
a-Naphth-	0.1	15.6	α-Naphthenyl	4.1	a-Naphthil	5.3
p-Tolu-	.25	30.0	p-Methylbenzyl	7.5	p-Tolil	7.0
p-Anis-	.25	34.0	*p*-Anisalcohol	10.0	*p*-Anisil	8.2
p-Bromobenz-	.25	45.3	p-Bromobenzyl	11.3	4,4′-Dibromobenzil	13.0
p-Chlorobenz-	.25	35.1	p-Chlorobenzyl	8.5	4,4′-Dichlorobenzil	8.4

Summary

Benzaldehyde is reduced by a mixture of magnesium and magnesium iodide to the iodomagnesium derivative of hydrobenzoin, $C_6H_5CH(OMgI)-(IMgO)HCC_6H_5$, thus using up two molecules of the aldehyde.

The iodomagnesium hydrobenzoinate so produced reacts immediately with a third molecule of the aldehyde, with formation of the salts of benzoin and benzyl alcohol, $C_6H_5COCH(OMgI)C_6H_5$ and $C_6H_5CH_2OMgI$.

The benzoinate salt suffers further, partial or complete, reduction by the binary system to tetraphenylerythritol and a polymer, or condensation product, of the latter.

Other aromatic aldehydes are affected by the binary system, i. e., by MgI, in a manner essentially similar to that in which benzaldehyde is affected.

ANN ARBOR, MICHIGAN

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[3] From a dissertation by R. V. Shankland, du Pont Fellowship holder, presented to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Science, 1930.

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

THE REDUCING ACTION OF COMPOUNDS CONTAINING THE GROUP >CHOMgI[1]

BY R. V. SHANKLAND AND M. GOMBERG

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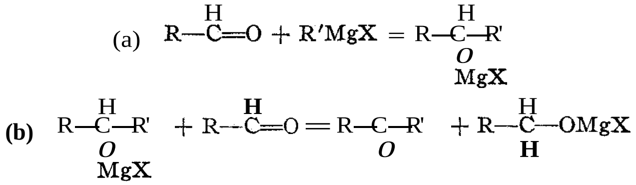
Aliphatic Grignard reagents have long been known to be capable of exerting a reducing action on aldehydes and ketones, the carbonyl group being reduced to a carbinol group while from the Grignard reagent saturated or unsaturated hydrocarbons, or both, were formed. In some of the cases, however, the by-product is neither saturated nor unsaturated hydrocarbon, and this is particularly so when aromatic Grignard reagents are employed. Instead, the oxidation product is a ketone, namely, that ketone which corresponds to the secondary alcohol which would be the result of the normal addition product of the aldehyde and Grignard reagent. Although several complicated theories have been proposed to account for the formation of these anomalous products, the mechanism of the reaction is, no doubt, relatively simple. In these cases, as was first shown by Marshall,[2] and as has been concurred in, finally, by Meisenheimer,[3] the reductions cannot be ascribed to the Grignard reagent itself, but rather to the primary normal addition product of that reagent with the aldehyde, according to the equation



$$\text{(a)}\quad R-\overset{H}{C}=O + R'MgX = R-\underset{\underset{MgX}{O}}{\overset{H}{C}}-R'$$

$$\text{(b)}\quad R-\underset{\underset{MgX}{O}}{\overset{H}{C}}-R' + R-\overset{H}{C}=O = R-\underset{O}{C}-R' + R-\underset{H}{\overset{H}{C}}-OMgX \qquad (1)$$

The oxidation and reduction reaction involves thus merely the transfer of H and MgX from one molecule to another, although the exact mechanism of this transfer still remains uncertain.

We converted secondary aromatic alcohols to their iodomagnesium derivatives and the latter were then treated with aldehydes. We found, in agreement with Meisenheimer's experiment on phenylethylcarbinol,[4] that the aldehydes were reduced to primary alcoholates, while the secondary alcoholates were oxidized to ketones.

The reducing action upon aldehydes, and also upon certain other compounds containing the carbonyl group, is not limited, however, to secondary

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[1] From a dissertation submitted by R. V. Shankland, holder of the du Pont Fellowship 1929–1930, to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Science, 1930.

[2] Marshall, *J. Chem. Soc.*, **105**, 527 (1914); **107**, 509 (1915); **127**, 2184 (1925).

[3] Meisenheimer, *Ann.*, **446**, 76 (1926).

[4] Ref. 3, p. 84.

alcohols; primary alcohols act more slowly, while dihydroxy secondary alcohols, glycols, are even more effective than monohydroxy secondary alcohols. Gomberg and Bachmann[5] found that the iodomagnesium derivative of hydrobenzoin reduces benzaldehyde to benzyl alcohol very rapidly, itself becoming oxidized to benzoin

$$C_6H_5CHO + C_6H_5CH(OMgI)(IMgO)CHC_6H_5 = C_6H_5CH_2OMgI + C_6H_5CO(IMgO)CHC_6H_5 \quad (2)$$

In other words, hydrobenzoin, although a di-secondary alcohol, functions in this reaction only through one of its two alcohol groups, just as if it were a monohydroxy alcohol. The ketone which results here, benzoin, can be isolated readily and the amount of it accurately established. This fact offered an opportunity to determine by means of hydrobenzoins on various aldehydes the extent of the possible occurrence of step (b) in Equation 1. Further quantitative evidence could thus be supplied in regard to Marshall's explanation concerning the apparently anomalous results in the Grignard reaction with aldehydes, especially when the aldehyde is employed in excess.

Experimental

Reduction of Benzaldehyde by **Iodomagnesium Hydrobenzoinate.**—The reduction of benzaldehyde by iodomagnesium hydrobenzoinate is very rapid. The rapidity of the reaction can be judged from the following set of experiments. Hydrobenzoin, prepared in 60% yield according to the procedure described by Danilov,[6] was converted into the iodomagnesium salt by adding 10.7 g. (0.05 mole) of the glycol to a standardized solution of ethylmagnesium iodide containing 0.1 mole of the Grignard reagent. To each sample was added a solution of 4.85 g. of benzaldehyde in benzene, and at the end of predetermined periods the reaction products were hydrolyzed and the components determined as described by Gomberg and Bachmann. The measure of oxidation–reduction that has occurred is based on the yield of benzoin. The results are given in Table I.

TABLE I

REDUCTION OF BENZALDEHYDE BY IODOMAGNESIUM HYDROBENZOINATE

Time	Temperature	Yield of benzoin Calcd., g.	Found, g.	%
5 Min.	Refluxing	9.70	7.10	73 2
15 Min.	Refluxing		9.2	95 3
30 Min.	Refluxing		8 95	92 3
5 Min.	Room temp.		5.82	00.0
30 Min.	Room temp.		8.40	86.6
4 Hrs.	Room temp.		8 45	87.1
42 Hrs.	Room temp.		9.05	93.3

Reduction of Various Aldehydes and of Ketones by **Hydrobenzoin.**—The reduction of aldehydes by iodomagnesium hydrobenzoinate proved to be a general method for the preparation of primary alcohols. The method might prove particularly useful in the preparation of primary unsaturated alcohols, since the ethylene bond remains unaffected

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[5] Gomberg and Bachmann, THIS JOURNAL, 52,4967 (1930).

[6] Danilov, *Ber.*, 60, 2393 (1927).

by the hydrobenzoinate salt. Although ketones, in general, proved unsuited for reduction by the glycolate, cyclohexanone and benzil were quantitatively reduced. The reduction of benzil by the glycolate is of especial interest as the oxidation product and reduction product are both iodomagnesium benzoinate. When acetophenone was treated with the glycolate a fair yield of benzoin was ohtained but no α-phenylethyl alcohol could be detected. Attempts to reduce p-dimethylaminobenzaldehyde by this method were unsuccrssful. Other methods of reduction are known to have failed in the case of that aldehyde; in fact, there is still some uncertainty as to the properties of *p*-dimethylaminobenzyl alcohol.[7] Iodomagnesium benzoate was not affected by the glycolate.

A summary of the results obtained appears in Table II. The solvent used in all experiments consisted of a mixture of one part absolute ether and two parts anhydrous benzene, and a total of 225 cc. of the solvent was used when 0.1 mole of the aldehyde was employed for the experiment, which amount was generally used except in Experiment 20, when 0.05 mole of each reactant was taken. In Experiment 7 hydrolysis was accomplished by means of ammonium acetate solution, while in Experiments 16, 17 and 18, water alone, followed by steam distillation, hydrolyzed the reaction product; in all other cases a mixture of ice and a slight excess of hydrochloric acid was used.

In Experiments 11 and 12, due to the relatively high boiling points of the alcohols formed, practically all of the benzoin was directly precipitated by adding petroleum

TABLE II

REDUCTION OF ALDEHYDES AND KETONES BY IODOMAGNESIUM HYDROBENZOINATE

	Carbonyl compound used	Yield of benzoin, g.	Yield of benzoin, %	Yield of alcohol, g.	Yield of alcohol, %
	Aldehydes				
1	Renzaldehyde	20.2	95.3	8.9	82.5
2	o-Tolualdehyde	19 0	89.6	10.0	81.9
3	*p*-Tolualdehyde	19 1	90 1	9.8	80.3
4	o-Anisaldehyde	18.3	86.3	9.6	69.6
5	p-Anisaldehyde	16.4	77 4	9.6	69.6
6	Piperonal	19.5	92.0	..	..
7	Salicylic aldehyde methoxymethyl ether	15.1	71.2	10.2	60.7
8	o-Chlorobenzaldchyde	18.8	88.7	12.5	88.7
9	p-Chlorobenzaldehyde	19 1	90.1	12.0	84.2
10	p-Bromobenzaldehyde	19 5	92.0	15.2	81.3
11	α-Naphthaldehyde	20 3	95.7	13.1	82.2
12	β-Naphthaldehyde	19 8	93.4	14.3	90.4
13	Phenylacetaldehyde	15 3	72.2	7.1	58.2
14	Cinnamic aldehyde	17.6	82.9	9.7	72.4
15	n-Heptaldehyde	16.5	77.8	7.6	65.5
16	Citronellal	16.6	78.3	10.7	68.6
17	Citral	15.8	74.5	10.1	65.6
18	Furfural	15.1	71.3	5.8	59.2
	Ketones				
19	Cycloliexanone	17.7	83.5	7.9	79.0
20	Benzil	20.5	96.7	..	..
21	Acetophenone	9.8	46.2	..	..

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[7] Clems and Smith, J. Chem. *Soc.*, 2423 (1928); Carothers and Adams, THIS JOURNAL, 46, 1675 (1924).

ether to the freshly hydrolyzed reaction product. After filtration, the solvents were removed by distillation and the residue was fractionated, yielding the alcohol. In Experiments **16** and 17 steam distillation separated the alcohol from the benzoin; the distillate was extracted with ether and benzene and the alcohol obtained from these by fractionation of the dried solution. In Experiment **18,** after the ether and benzene were removed by steam distillation, the residue in the distilling flask was filtered from the water, the solid was washed with warm water and the aqueous filtrate extracted with ether and benzene. The furfuryl alcohol was obtained by distillation of the ether–benzene extract In Experiment 6, although good yields of benzoin were obtained, none of the pure alcohol to correspond to piperonal could be isolated. Apart from these exceptions, all experimental details were similar to those described under the reduction of benzaldehyde, and the alcohols formed were separated from the benzoin by distillation under highly diminished pressure. The alcohols were identified by their boiling points, mixed melting points if solid and by their naphthylurethans.

Reductions by Substituted **Hydrobenzoins.**—A summary of these reductions is given in Table III. Equimolecular quantities of oxidizing agent and reducing agent were used in each experiment. Since *p*-toluoin, unlike benzoin, is very soluble in ether and benzene, none precipitated on hydrolysis of the reaction mixture. The ether–benzene solution, after hydrolysis, was fractionated under reduced pressure; after the alcohol had distilled the p-toluoin came over at 210° under a pressure of **1** mm., and was finally purified by crystallization from alcohol. Dichlorobenzoin is also quite soluble in all ordinary solvents. After the alcohol had been distilled, the residue was dissolved in boiling benzene; on cooling the solution, **0.35** g. of the 4,4'-dichlorobenzil, m. p. 195°, separated, due to the ready oxidation of the benzoin by air. The benzene was removed by distillation and the residue was dissolved in boiling aqueous alcohol, an atmosphere of nitrogen being maintained over the surface of the liquid. On cooling, the dichlorobenzoin crystallized in the form of fine needles. In the experiment with methylhydrobenzoin, the reaction product was hydrolyzed as usual and the ether-benzene solution was extracted with a saturated solution of sodium bisulfite, after which the organic solvents were allowed to evaporate spontaneously. The residual mass was digested with cold water until partial solidification took place. The mixture was filtered through a sintered glass filter. From the solid, recrystallized, the methylbenzoin, melting at 65.6°,[8] was obtained; the liquid yielded the corresponding benzyl alcohol. Under similar conditions of experiment, phenylhydrobenzoin, as well as tetraphenylerythritol, did not reduce aldehydes.

TABLE III

REDUCTION OF ALDEHYDES BY SUBSTITUTED HYDROBENZOINS

Hydrobenzoin used	Benzaldehyde reduced	Benzoin obtained	Yield. %	Yield of alcohol obtained, %
4.4'-Dimethyl-	4-Methyl-	4,4'-Dimethyl-	84.6	81.8
4,4'-Dimethyl-	2-Chloro-	4,4'-Dimethyl-	83.3	84.8
4,4'-Dimethyl-	4-Chloro-	4,4'-Dimethyl-	82.5	81.2
4.4'-Dichloro-	2-Chloro-	4,4'-Dichloro-	85.8	82.5
a-Methyl	Benzald	a-Methyl-	64.2	51.5

Reductions by Iodomagnesium Derivatives of Secondary Alcohols.—A summary of the results obtained with benzhydrol as the reducing agent appears in Table IV. Besides reducing aldehydes, this alcohol was found capable of reducing benzil also, to idomagnesium benzoinate. The oxidation product was in all cases benzophenone; that the ketone was formed directly as such was proved by the fact that when the still

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[8] Roger, *J. Chem. Soc.*, 12'7, 518 (1925).

unhydrolyzed reaction product was subjected to the action of the binary system $MgI_2 + Mg$, good yields of benzopinacol were obtained.[9] Since the pinacol is quite insoluble in alcohol and could therefore be separated readily from other products of the reaction, the treatment with the binary system afforded a better method of estimating the yield of ketone formed than isolation of benzophenone itself. In the case of the reduction of benzil by the iodomagnesium derivative of benzhydrol, since the binary system would attack both benzil and iodomagnesium benzoinate, that method of estimating the yield of benzophenone was not used. One-tenth mole of each reactant was used except in Experiment 6, in which case 0.05 mole of each reactant was taken.

TABLE IV

REDUCTION BY BENZHYDROL

	Carbonyl compound reduced	Yields Benzophenone, %	Yields Alcohol, %
1	Benzaldehyde	83.7	71.7
2	*p*-Tolualdehyde	80.8	72.2
3	o-Chlorobenzaldehyde	71.7	73.0
4	p-Chlorobenzaldehyde	79.7	75.8
5	p-Bromobenzaldehyde	77.5	72.7
6	Benzil	82.4	79.2 (benzoin)

Table V contains the yields of the products obtained when the iodomagnesium derivatives of two other secondary alcohols were used as reducing agents. The reaction of the iodomagnesium derivative of benzpinacolin alcohol with benzaldehyde was of especial interest, as it furnished the explanation why Schmidlin[10] and Chichibabin[11] failed to obtain benzopinacolin alcohol (unsym.-tetraphenyl alcohol) by the action of triphenylmethylmagnesium halides on benzaldehyde, the explanation being that the excess of aldehyde oxidized the alcohol so formed to the corresponding ketone, *i. e.*, the pinacolin

$$C_6H_5CHO + C_6H_5CH(OMgCl)C(C_6H_5)_3 = C_6H_5CH_2OMgCl + C_6H_5COC(C_6H_5)_3$$

Our low yields of acetone, obtained when iodomagnesium isopropylate was used, were due to the occurrence of condensations of aldehyde with the acetone formed in the reaction; in fact, styryl methyl ketone, 7 g., was isolated in the experiment with benzaldehyde. The amounts of the reducing alcohols used were 0.05 mole.

TABLE V

REDUCTION BY VARIOUS SECONDARY ALCOHOLS

Secondary alcohol	Aldehyde	Oxidation product	Yield, %	Reduction product, alcohol	Yield, %
Benzopinacolin	Benz-	Benzopinacolin	80.0	Benzyl	78.0
Benzopinacolin	o-Chlorobenz-	Benzopinacolin	77.3	o-Chlorobenzyl	75.0
Isopropyl	Benz-	Acetone	30.0	Benzyl	52.0
Isopropyl	o-Chlorobenz-	Acetone	20.4	o-Chlorobenzyl	71.0

Reductions by **Iodomagnesium** Derivatives of Primary Alcohols.—Primary alcohols, in the presence of a small amount of aluminum, or halogenomagnesium, alcoholate salt as catalyst, are known to be capable of reducing aldehydes and some other carbonyl compounds[12]

$$RCH_2OH + R'CHO \rightleftharpoons RCHO + R'CH_2OH$$

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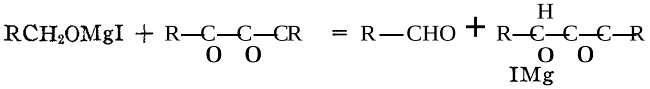
[9] Gomberg and Bachmann, THIS JOURNAL, 49, 2361 (1927).

[10] Schmidlin, *Ber.*, 39, 4183 (1906).

[11] Chichibabin, *ibid.*, 42, 3469 (1909).

[12] Meerwein and Schmidt, *Ann.*, 444, 221 (1925).

This reaction is reversible, but if, for instance, iodomagnesium benzylate be treated with a susceptible carbonyl compound whose reduction product is not affected by benzaldehyde, then the reaction should go to completion. Benzils are such compounds



$$RCH_2OMgI + R-\underset{O}{C}-\underset{O}{C}-CR = R-CHO + R-\overset{H}{\underset{\underset{IMg}{O}}{C}}-\underset{O}{C}-C-R$$

In two experiments of this nature, using benzyl and chlorobenzyl alcohol, respectively, and benzil as the oxidizing compound, we obtained an 85% yield of the corresponding aldehydes and 90% of benzoin.

Summary

To a still greater extent than the iodomagnesium salts of monohydroxy alcohols, the similar salts of hydrobenzoin and of substituted hydrobenzoins have been found effective in reducing saturated and unsaturated, aromatic and aliphatic aldehydes to their corresponding primary alcohols. Only one of the two alcohol groups in the hydrobenzoins is involved in this reaction, the hydrobenzoins becoming oxidized by the aldehydes to benzoin~just as secondary alcohols become oxidized to ketones.

The mechanism of this oxidation–reduction reaction consists in the transfer of an H and MgI from the group >CHOMgI in the alcohol to the carbonyl group of the aldehyde.

The results of this investigation supply further evidence in favor of Marshall's explanation in regard to the apparently anomalous formation of primary alcohols and ketones in the course of the Grignard reaction on aldehydes: namely, the normally produced addition product, RR'CHOMgI, is liable to become oxidized by the excess of aldehyde to the ketone RCOR', and the aldehyde reduced to RCH_2OMgI.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PYROLYSIS OF PROPYLENE[1]

BY CHARLES D. HURD[2] AND RICHARD N. MEINERT[3]

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That hydrocarbons of different types differ quite widely from each other in their behavior on pyrolysis has been demonstrated in earlier papers of this series. Normal and isobutane[4] both undergo primary changes into

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[1] This paper contains results obtained in an investigation on "The Pyrolysis of Pure Hydrocarbons," listed as Project No. 18 of American Petroleum Institute Research. Financial assistance in this work 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).

simpler substances. Isobutylene[5] not only yields simpler gaseous products but also gives rise to liquids which are aromatic in character. Methylacetylene was found to rearrange into allene, and allene,[6] in turn, pyrolyzes almost exclusively into allene polymers. These polymers are liquids of an entirely different nature from the liquids produced from isobutylene.

The subject of this study, propylene, has been investigated previously only by Frey and Smith.[7] They observed that about one-third of the propylene was decomposed at 575° with a reaction time of four minutes, in a silica bulb. Among the products of the reaction were hydrogen, ethylene, ethane and propane in small amounts. They also reported the presence of butylene and of small amounts of paraffin hydrocarbons containing as high as eight carbon atoms. The same workers showed that propylene reacts with hydrogen at 575° to form some propane.

Preliminary experiments in this Laboratory[8] indicated that propylene was not appreciably changed at temperatures below 525° in pyrex glass apparatus when the hot contact time was fifty seconds. The present study revealed that there was practically no change below 600° even with contact times of two minutes. At 600' the change was only 4% with a contact time of thirty seconds but it increased to about 30% with a contact time of 158 seconds. At 650° and 120 seconds the amount of propylene pyrolyzed was 60%, while at the same temperature and a contact time of thirty seconds it was 16%. At 700° the change was 51% with a contact time of only twenty-five seconds, but it reached 72.5% by doubling the contact time. In quartz tubes with a contact time of about one-half second, the propylene was 90 to 95% pyrolyzed when the temperature was 900 to 950°. The course of the reaction was similar to the results in pyrex wherein a lower temperature but a longer contact time was used.

The reaction in pyrex was predominantly homogeneous and unimolecular, since dilution of the gas with nitrogen, or creation of an increased surface by packing the tube with pyrex glass, had a negligible effect on the fraction of propylene decomposed in a given time.

The larger part of the propylene which disappeared in the reaction was broken down into simpler gases. Methane, ethylene, hydrogen and paraffins higher than methane (consisting principally of ethane) were found in the ratio of 3:3:1:1. As would be expected, the quantity of methane, hydrogen and total gas was found to increase with increasing temperature or with increasing contact time. This is evidently due not only to a greater extent of pyrolysis but also to secondary reactions which involve the breakdown of C_2 hydrocarbons.

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[5] Hurd and Spence, THIS JOURNAL, 51,3561 (1929).

[6] Meinert and Hurd, *ibid.*, 52, 4540 (1930).

[7] Frey and Smith, Ind. *Eng. Chem.*, 20, 948 (1928).

[8] Hurd and Spence, unpublished results.

In pyrex or in quartz about one-fifth to one-fourth of the propylene used was converted into aromatic liquids. Benzene and toluene were identified and more complex substances, such as naphthalene and phenanthrene, were indicated. The last two are not considered to be primary products of the pyrolysis since they could arise by interaction of the simpler aromatic hydrocarbons with olefins at the high temperatures in question.

When small volumes of propylene were pyrolyzed no feasible method suggested itself of obtaining the weight of the liquids, but with larger runs this could be done although quantitative precision was, necessarily, not realized. Thus, it was possible to account for the hydrogen within fairly satisfactory limits. In two runs at 700°, the check was 100–104% of the theoretical and in one run at 955° the value was 107%. In one run at 650° only 88% of the hydrogen was accounted for, and in one at 600° the value dropped to 81%. Probably these variations are the result of experimental error due to the smaller quantity of liquid product which was formed in these lower temperature experiments. Similar calculations on the carbon balance were of value in estimating the limit for the quantity of carbon which may have been liberated in the various runs.

When a mixture of approximately equal parts of hydrogen and propylene was pyrolyzed, it was noticed that the amounts of ethylene and methane formed were greatly increased. Little or no propane was formed. This indicates a tendency for the hydrogen to cause a scission of the propylene molecule, thus

$$CH_3{-}CH{=}CH_2 + H_2 \longrightarrow CH_4 + CH_2{=}CH_2$$

Such a reduction may be preceded by the division of propylene into the methyl and vinyl radicals.

The pyrolytic behavior of propylene in monel metal was also investigated. Here the almost exclusive change was a decomposition into hydrogen and a sooty form of carbon. Moreover, the rate of decomposition was much greater than when pyrex or quartz tubes were employed. Thus, with the same hot contact periods, much more propylene decomposed in monel at 350° than in pyrex at 650°.

A peculiarity about the reaction in monel metal was that it was autocatalytic. The carbon formed and deposited on the walls of the tube near the beginning of the experiment catalyzed the reaction so that it proceeded much more rapidly after about twenty minutes. A number of experiments at different temperatures showed conclusively that this was the case. Both in appearance and in quantity was the carbon from the monel tube in decided contrast to the shiny, hard flakes of carbon which were deposited on the walls of the pyrex tube.

The pyrolysis in monel metal tubes started at a temperature of 350°. At 375°, with a contact time of about half a minute, it was practically complete. No liquids or tarry products were formed in the reaction at any temperature from 300 to 650°. About one liter of hydrogen and one-half liter of a mixture of paraffin hydrocarbons resulted from each liter of propylene consumed at 375°. With increasing temperature, the amount of hydrogen formed per liter of propylene increased to 1.7 liters at 650°, while the amount of paraffins (chiefly methane) formed decreased to 0.2 liter.

The fact that the production of hydrogen increased with increasing temperature while the production of paraffins decreased indicates that the first step in the reaction is probably a splitting into compounds that are simpler than propylene, but which are themselves unstable at higher temperatures and also break down into their elements.

Propylene, Isobutylene and Allene Compared.—It is interesting to compare the relative stability in pyrex of propylene and isobutylene, since both are olefin hydrocarbons which have been studied under analogous conditions. In Table I it is shown that at the same temperature and contact time, the amount of pyrolysis is about the same for the two hydrocarbons. The isobutylene data are from the paper of Hurd and Spence.[9]

TABLE I

RELATIVE STABILITY OF PROPYLENE AND ISOBUTYLENE

Isobutylene			Propylene		
Temp., °C.	Contact time, sec.	Extent of pyrolysis, %	Temp., °C.	Contact time, sec.	Extent of pyrolysis, %
600	200	20.0	600	190.0	24.3
650	27	22.7	650	26.8	16.7
			650	30.0	16.0
700	25	51.4	700	25.0	50.8

The mechanism which has been developed for isobutylene adequately explains the data in the pyrolysis of propylene. The former was reported to produce methane, propylene, hydrogen and isobutane at 600° in the ratio (approximately) of 10:5:3:4. At 700° there was more methane and considerably less propylene in the off-gas. From the results obtained in this work, it would be expected that propylene formed from isobutylene would break down rather rapidly at 700°. Aromatic liquids were found to the extent of 23 to 63%, depending on the temperature and the contact time. Similar liquids were formed from propylene in 15–28% yields.

To explain the pyrolysis of i-butylene, Hurd and Spence suggested that heat may rupture the single C—C or C—H bonds and that it may activate the C=C double bonds. Gaseous products were regarded as coming from the first process and liquids from the last. Evidently the same mechanism applies with the pyrolysis of propylene. The general experimental data for both propylene and isobutylene were very similar.

Propylene and allene are both C_3 hydrocarbons, but their mode of pyrolysis is quite different. The former is considerably the more stable of

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[9] Hurd and Spence, THIS JOURNAL, **51**, 3561 (1929).

the two and it changes into gases and aromatic liquids. The latter gives but small amounts of gases and large quantities of non-aromatic liquids. No allene or polymers of allene were found (except possibly in traces) among the products of pyrolysis of either propylene or isobutylene.

Experimental Part

Apparatus.—An apparatus similar to the one described by Hurd and Spence for use with *i*-butylene[10] was constructed for this study. The dimensions of the various reaction tubes were as follows:

Tube	Total length, cm.	Inside diameter, cm.	Length in furnace, cm.
Pyrex	90	2.5	75
Quartz	85	0.45	75
Monel	92	2.0	75

A 15-cm. length of 7-mm. tubing was sealed into the bottom of the pyrex tube. It was attached to a trap immersed in ice water which served to condense the liquid products of the reaction. The thermocouple was placed inside the pyrex tube and was protected by a pyrex sheath.

Temperature measurements of the quartz tube were made by placing the thermocouple in another quartz tube having walls of the same thickness and having one end closed. The two tubes were suspended side by side in the furnace with the end of the thermocouple about two-thirds of the way down.

With the monel metal tube the thermocouple was placed inside the tube with a porcelain insulator as its only covering. The ends of the thermocouple were exposed directly to the hot gases and the leads were run through the rubber stopper which closed the top end of the tube. To prevent the conduction of heat to the rubber stoppers, tight spiral coils, consisting of right turns of 5-mm. copper tubing, were wound around both ends of the monel tube. With water circulating through these coils the ends of the monel metal tube were kept quite cool by this device.

The gases were analyzed as previously outlined by Hurd and Spence.[11]

Source of Propylene.—The propylene used in these experiments was generously furnished by E. R. Squibb and Sons. Analysis showed that it contained less than 1% of impurities.

The Pryolysis of Propylene in Pyrex.—Preliminary experiments, with temperature varying between 550 and 700° and the contact time varying between twenty-five and one hundred fifty seconds, were made to determine the best conditions for the pyrolysis. The results are given in Table II, and the data make it evident that increasing either the temperature or the contact time gives rise to a marked increase in the amount of propylene decomposed. The results show further that the temperature range between 600 and 700° offers the best opportunity for studying the mechanism of the reaction. Below 600° the pyrolysis is negligible, while above 700° the reaction is complicated by secondary reactions, consisting of the decomposition of the products of the primary reactions.

It will be noted that the relative amounts of the various products formed

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[10] Hurd and Spence, THIS JOURNAL, 51, 3562–3563 (1929).

[11] Hurd and Spence, *ibid.*, **51,** 3356–3357 (1929).

TABLE II

EFFECT OF TEMPERATURE AND RATE OF FLOW

Run number	2	3	4	6	5	7	8
Temperature, °C.	600	650	700	550	600	650	700
Contact time, sec.	29	30	25	137	158	120	52.4
Decomposition, %	3.9	16	50.8	4.1	29.7	59.3	72.5
Cc. of products formed per liter of propylene pyrolyzed							
Absorbed in 62.5% H_2SO_4	...	59	24	...	7	0	0
Acetylenes	...	32	11	...	16	6	0
Ethylene	...	314	396	...	269	323	438
Hydrogen	...	83	149	...	69	127	152
Paraffins	...	415	558	...	375	637	580

from each liter of propylene pyrolyzed are not greatly affected either by changing the temperature or the contact time. This matter will be discussed in more detail in a later section.

Effect of Dilution on **the** Reaction.—Several runs were made with either hydrogen or nitrogen added to the propylene in order to find out the effect of dilution of the propylene. The results are shown in Table III.

TABLE III

EFFECT OF DILUTION ON THE PYROLYSIS OF PROPYLENE

Run number	5	12	11	10
Temperature	600°	600°	600°	600°
Contact time, sec.	158	158	125	125
Per cent. propylene in entering gas	97	53.1	97	56.6
Per cent. N_2 in entering gas	00	45.7	00	00
Per cent. H_2 in entering gas	00	00	00	39.1
Per cent. propylene pyrolyzed	29.7	23.3	26.7	29.5
Products formed per liter of propylene pyrolyzed, cc.				
Gas removed by 62.5% H_2SO_4	7	12	22	00
Acetylenes	16	16	49	22
Ethylene	269	428	340	560
Hydrogen	69	130	119	[a]
Paraffins	375	500	388	747
n in C_nH_{2n+2}	1.54	1.42	1.42	1.25

[a] 387 cc. of hydrogen were used up for each liter of propylene pyrolyzed.

Examination of Runs 5 and 12 shows a somewhat smaller percentage of pyrolysis in the latter case. Whether or not this is a significant difference is open to question since in high temperature experiments which are carried out under seemingly identical conditions it is the customary experience that precise duplication of data is only rarely achieved. We are inclined to believe that the values 29 and 23 are sufficiently near each other to indicate a predominantly unimolecular reaction, although strict interpretation of the values would indicate a reaction order between first and second. Some of the other differences which are noticeable in these two runs may be accounted for by the fact that in Run 12 almost no liquid reaction products were formed whereas in Run 5, with no dilution, about 20% of the propylene pyrolyzed was recovered as liquids. The nitrogen would act to lessen the formation of liquids by diluting the primary reaction products and hindering them from undergoing polymerization.

When Runs 10 and 11 are compared, the percentage of pyrolysis is a little higher (rather than lower) in the dilution experiment. The order of magnitude is similar, however. As in the nitrogen dilution experiment, the amounts of ethylene and of paraffins formed are much larger than in runs where there was no dilution. Again, with a smaller liquid yield, the gaseous products showed up correspondingly when calculated on the basis of cc. of each product formed per liter of propylene pyrolyzed.

A striking result when Runs 11 and 10 are compared is the change in the n in the paraffin formula. The volume of the paraffins formed is greatly increased, relatively more so than the volume of ethylene, but the n is decreased by adding hydrogen to the entering gas. This indicates the formation of methane, probably by hydrogenation of the CH_3- radicals formed when the propylene is split at the single bond. Apparently not much propylene is hydrogenated to propane; otherwise the n would be higher than it is. This is an important point when considering the mechanism of the reaction, for it is best interpreted by considering that the CH_3- residue is present in the hot zone, at least momentarily.

Effect of Increased Surface.—Experiments were made at 600 and 650° to determine whether or not increasing the surface in the reaction tube had any effect on the amount of propylene pyrolyzed. The method consisted of packing the tube with long pieces of capillary tubing made by heating sections of large capillary tubing and drawing them out to a diameter of about one millimeter. Rough calculation showed that the surface in the reaction tube was about trebled. Table IV shows the results of the experiments. The calculation for the contact time took account of the decrease in the volume of the tube due to the packing. Evidently the increased surface in the tube had no appreciable effect upon the amount of propylene pyrolyzed. Therefore, the decomposition of propylene is apparently unimolecular and homogeneous.

TABLE IV

EFFECT OF INCREASED SURFACE

	Unpacked	Packed	Unpacked	Packed
Run number	20	25	21	26
Temperature, °C.	600	600	650	650
Contact time, sec.	139	150	90.2	115
Percentage pyrolysis	18.7	17.0	41.8	44.2

Gaseous Products Obtained in the Reaction.—The gaseous products of the pyrolysis of propylene were measured, collected and analyzed. From the percentage of propylene in the off-gas, the amount of undecomposed propylene was determined, and this, subtracted from the propylene passed into the tube, gave the amount of propylene changed in the pyrolysis. The percentage of pyrolysis could then be readily calculated.

From the analysis of the off-gas and the volume of the off-gas, the total volume of each component present was found. This was divided by the number of liters of propylene actually changed and the result expressed as the number of cc. of each component per liter of propylene pyrolyzed. The advantage of this method of calculating the results is apparent, for it puts all the experimental data on *a* common basis.

Table V shows some of the representative data at various temperatures and contact times. The table includes data with both pyrex and quartz reaction tubes.

TABLE V

PRODUCTS OBTAINED FROM PROPYLENE PYROLYZED IN PYREX AND QUARTZ

Run number	5	11	24	3	7	23	4	8	28	29
Tube, pyrex or quartz	P	P	P	P	P	P	P	P	Q	Q
Temp., °C.	600	600	600	650	650	650	700	700	950	955
Contact time, sec.	158	125	131	30	120	79	25	53	0.513	0.471
Entering flow, cc./min.	43	52	51	217	53	80	237	115	311	339
Exit flow, cc./min.	39	51	50	207	55	80	261	130	436	478
Press. in tube, mm.	744	750	752	748	746	750	744	742	744	750
Vol. entering gas, l.	9.56	23.3	3.73	23.9	10.1	3.84	24.9	13.7	12.44	17.96
Vol. exit gas, l.	8.87	22.7	3.63	23.7	10.5	3.85	26.8	15.5	17.45	25.33
C_3H_6 in entering gas, %	94.9	96.8	95.9	96.6	95.3	95.9	94.2	95.2	95.0	95.0
Composition of exit gas, percentage by volume										
Acetylenes	1.3	1.5	0.0	0.9	1.1	1.1	1.8	1.4	2.2	2.4
Absorbed in 62.5% H_2SO_4	1.3	1.4	0.0	2.1	0.9	1.1	2.1	0.6	1.2	0.3
Propylene	71.9	72.6	83.4	82.0	37.1	59.2	43.0	23.0	6.7	3.3
Ethylene	8.2	9.0	5.2	4.9	17.5	12.9	17.7	26.7	23.5	24.4
Hydrogen	2.1	2.9	1.3	1.3	6.9	4.3	6.6	9.3	22.0	24.7
Paraffins	11.4	10.3	6.4	6.5	34.5	18.6	24.8	35.2	41.0	43.2
n in C_nH_{2n+2}	1.5	1.42	1.54	1.3	1.25	1.29	1.2	1.16	1.05	1.09
Carbon monoxide	0.4	1.0	0.2	0.5	0.6	0.2	0.0	1.1	....	....
Carbon dioxide	.4	0.0	.0	.2	.1	.3	.3	.2	....	....
$CO + CO_2$	....	....	....	...	....	....	...	....	0.9	0.8
Pyrolysis, %	29.7	26.7	15.5	16.0	59.3	38.4	50.8	72.5	90.3	95.2
Cc. of gaseous products formed per liter of propylene entering										
Acetylenes	5	13	....	5	4	....	6	....	31.8	34.8
Absorbed in 62.5% H_2SO_4	2	6	....	9	3	....	12	....	17.4	3.8
Ethylene	80	91	53	50	192	134	202	318	343.0	354.5
Hydrogen	21	32	13	13	76	45	76	111	318.0	359.0
Paraffins	112	104	65	67	378	194	283	420	593	628
Cc. of gaseous products per liter of propylene pyrolyzed										
Acetylenes	16	49	....	32	6	....	11	....	35.2	36.6
Absorbed in 62.5% H_2SO_4	7	22	....	59	5	....	24	....	19.3	4.0
Ethylene	269	340	340	314	323	350	396	438	379.6	372.7
Hydrogen	69	119	85	83	127	117	149	152	352.3	377.3
Paraffins	375	388	418	415	637	505	558	580	656.5	659.9
Wt. of liquids, g.	Trace	2.37	....	Trace	1.7	....	6.9	3.8	....	6.47
Per cent. of liquids, by wt. of C_3H_6, pyrolyzed	....	21	....	...	15.4	....	27.6	24	....	20.8

Sufficiently large samples of propylene were used in Runs 11, 7, 4, 8 and 29 so that it was possible to check the hydrogen (free or combined) in the final gaseous products with the combined hydrogen in the original propylene, correction being made in the latter for the propylene which was found to change into liquid products. In these runs the liquid could be weighed satisfactorily although high precision in this regard was impossible. This, no doubt, was the major cause for the discrepancies which were noted in the hydrogen balance. In Runs 5, 24, 3 and 23 the original quantity of propylene was too small to yield a satisfactory volume of liquid. In Run 28 the liquid product was not worked up.

In Run 11, 1906 out of a possible 2370 units of hydrogen were found in the gaseous products per liter of propylene pyrolyzed; in Run 7, 2233 out of 2538; in 4, 2276 out of 2172; in 8, 2281 out of 2280; and in 29, 2553 out of 2376. In making these calculations, the gas which was "absorbed in 62.5% H_2SO_4" was assumed (with no especial justification) to be C_4H_8, and the "acetylenes" were assumed to be C_2H_2. To illustrate the method of calculation in Run 11, 49 cc. of $C_2H_2 \Bumpeq$ 49 cc. of H_2; 22 cc. of $C_4H_8 \Bumpeq$ 88 cc. of H_2; 340 cc. of $C_2H_4 \Bumpeq$ 680 cc. of H_2; 388 cc. of $C_nH_{2n}+$, where $n = 1.42 \Bumpeq$ 970 cc. of Hz, which with 119 cc. of H_2 totals 1906 cc. Supposedly, this volume originated from 79% of 1000 cc. of C_3H_6, which is equivalent to 2370 cc. of hydrogen. The check is only 81% of the theoretical, but in the other four cases it is better, namely, 88, 104, 100 and 107%.

The carbon content of the gaseous products was always less than the carbon content of the original propylene, corrected as before for the portion which changed into liquids. The two chief causes for this difference were carbon formation and the experimental difficulty in collecting and weighing the small volume of liquid. Thus, in Runs 11, 7, 4, 8 and 29 the units of carbon in the gas at the end and at the beginning, respectively, were 1417/2370, 1474/2538, 1580/2172, 1514/2280, 1553/2376. If these differences are interpreted as being solely due to carbon formation, the values would indicate, respectively, 0.51, 0.57, 0.32, 0.41 and 0.45 g. of carbon.

The Liquid Portion.—In addition to the gaseous products, about 20% by weight of each liter of propylene pyrolyzed was recovered as liquid products. In the cases where the temperatures were low and the contact time short, the decomposition of the propylene was very small; consequently it was difficult to weigh the liquids which were obtained, as they amounted to less than a gram, and some of the liquid stuck to the walls of the reaction tube. But with three runs, one at 650° with a contact time of 150 seconds, and two at 700° and a contact time of thirty-six and fifty-two seconds, respectively, several grams of liquids were obtained and these runs averaged a liquid formation of 22% by weight of the propylene actually pyrolyzed.

A portion (12.5 g.) of these liquids, being the aggregate of several runs, was fractionated with a Vigreux fractionating column. The results were as follows.

Fraction number	Roiling point, °C	Weight, g.
1	70–85	2.34
2	85–107	2.04
3	107–160	2.41
4	160–200	1.58
5	200–210	0.90
Residue		2.90
Loss		0.31
		12 48

Fraction 5 partially solidified on cooling. All these fractions had an aromatic odor resembling that of toluene.

Fractions 1, 2 and 3 were fractionated into three fractions and the refractive indices of these portions were determined. For reference, the refractive index of benzene, n_D^{20}, is 1.501, and for toluene, 1.495.

Fraction	Boiling point, °C.	n_D^{20}
A	75	1.490
B	75–85	1.499
C	85–128	1.502

Most of the fraction B boiled between 83 and 85° and most of fraction C boiled above 118°. The refractive indices, together with the boiling points, indicate that these compounds are aromatic, presumably benzene and toluene with some higher homologs. Fraction A and B nitrated readily and, in experiments described below, it was confirmed that the former was the nitro derivative of benzene. The higher-boiling fractions could not be obtained pure and were not identified.

Besides the gaseous and liquid products, there was always a thin deposit of carbon formed in the reaction tube. This carbon was in the form of graphite and could be removed by scraping it from the tube, but it was more completely removed before each run by burning it out. There was also a small amount of heavy tar which collected on the sides of the tube, which was removed from time to time by dissolving it out with acetone.

The Effect of Shorter Contact Times and Higher Temperatures upon the Pyrolysis of Propylene.—The results are summarized in Runs 25 and 26 of Table V. A quartz tube was used instead of the pyrex tube. The gas was passed through the apparatus as rapidly as possible so that the hot contact time would be very short. The temperature was 950°. This was the maximum temperature of the furnace.

Comparison of these runs with the others shows that pyrolysis at 950° in quartz with a hot contact time of one-half second gives about the same results as pyrolysis at 700° in pyrex with a contact time of fifty-three seconds. The percentage of propylene pyrolyzed is about 90 instead of 73, but the products formed are very much the same. There is about the same percentage of unrecovered propylene which is converted into liquids in each case, *viz.*, 20–25%. In both cases liquids are aromatic hydrocarbons and in both the gaseous products are the same. More hydrogen and methane are formed at the higher temperatures but this would be expected, since the secondary reactions would also be more rapid at high temperatures.

The liquids obtained from the 950° experiments were fractionally distilled as carefully as the small volume would permit, with these results.

Fraction	Volume, cc.	B. p., °C.	n_D^{20}
A	2.0	78–97	1.5025
B	0.8	97–130	1.5140
C	1.0	130–180	1.5465

Fraction A had an odor very much like that of benzene, fraction B an odor somewhat resembling that of toluene and fraction C smelled like tar. The properties of these liquids were almost identical with those of the liquids obtained from propylene in pyrex apparatus at 700°. Nitration of fraction A yielded m-dinitrobenzene.

Experiments with a Monel Metal Tube.—A summary of data is given in Table VI. It will be seen that the effluent reaction products were gaseous, but in addition there was always a large amount of carbon deposited in the tube. In some cases this deposit was so thick that it closed

TABLE VI

PRODUCTS OBTAINED FROM PROPYLENE IN MONEL METAL TUBE

Run	1	2	3	4	5	6	7
Temp., °C.	650	500	375	250	325	350	400
Contact time, sec.	14.8	35.3	27.3	22.7	26.5	25.8	10.5
Entering flow, cc./min.	174	90	139	207	169	166	377
Exit flow, cc./min.	362	175	225	207	170	220	523
Press. in tube, mm.	745	748	752	742	748	745	741
Vol. entering gas, l.	5.32	2.25	7.63	16.55	10.68	6 65	11.30
Vol. exit gas, l.	11.05	4.38	12.35	16.55	10 77	8.80	15.6
C_3H_6 in entering gas, %	94.7	94.7	94.7	94.7	94.7	94.7	94.75
Composition of exit gas, percentage by volume							
Hydrogen	77.6	71.3	56.8	...	....	38.3	39.9
Propylene	2.9	1.0	4.8	93.7	94 3	37.6	46.2
Ethylene	2.4	1.0	0.6	....	....	0.3	1.0
Other unsatd. hydrocarbons	1.1	2.0	2.1	...	....	0.5	1.2
Paraffins	9.2	13.0	30.0	....	....	21.7	9.1
n in C_nH_{2n+2}	1.26	1.50	1.54	...	...	1.81	1.83
Percentage pyrolysis	93.6	92.7	91.2	0.0	0.5	47.4	32.4

TABLE VI (*Concluded*)

Gaseous products formed per liter of propylene entering, cc.						
Hydrogen	1620	1390	976	....	....	535	583
Paraffins	192	253	514	....	....	303	133
Ethylene	60	19	10	....	....	4.2	14
Other unsatd. hydrocarbons	27	39	35	....	....	7	17
Gaseous products formed per liter of propylene pyrolyzed, cc.						
Hydrogen	1730	1500	1070	....	...	1128	1800
Paraffins	205	273	564	. ..	. ..	638	411
Ethylene	64	21	11	....	....	9	45
Other unsatd. hydrocarbons	29	42	38	....	....	15	54

the tube completely and stopped the flow of the gas. This carbon was not graphitic as was the carbon deposited when propylene was pyrolyzed in a pyrex tube, but it had the appearance of soot and could be scraped easily from the walls of the tube. No liquids were obtained.

It was noticed in these experiments that the ratio of the off-gas to the entering gas began to increase after the first five or ten minutes of the run and finally reached a constant value. This points to the fact that the action is autocatalytic, the carbon deposited on the walls acting as the

TABLE VII

RATIO OF OFF-GAS TO ENTERING GAS IN MONEL METAL

		Run 1, 650°						Run 3, 375°			
Time	**Entering volume**	**(a)**	**Exit volume**	(*b*)	**Ratio** *b/a*	**Time**	**Entering volume**	(*a*)	**Exit volume**	(*b*)	**Ratio** *b/a*
0	0.000	...	0.000	...	..	0	0.000	...	0.000	...	..
3	.020	0.020	.032	0.032	1.60	3	.015	0.015	.015	0.015	1.00
8	.057	.037	.106	.074	2.00	13	.072	.057	.077	.062	1.09
13	.097	.040	.185	.079	1.97	18	.102	.030	.117	.040	1.33
23	.161	.064	.341	.156	2.44	28	.160	.058	.202	.085	1.46
28	.190	.029	.407	.066	2.27	38	.220	.060	.294	.092	1.53
30	.198	.008	.424	.017	2.13	43	.248	.028	.344	.050	1.78
						53	.306	.058	.440	.096	1.66
						63	.362	.056	.537	.097	1.73
						68	.394	.032	.591	.054	1.69
		Run 6, 350°						**Run 7, 400°**			
0	0.000	...	0.000	...	..	0	0.000	...	.000	...	..
5	.033	0.033	.036	0.036	1.09	4	.055	0.055	.055	0.055	1.00
10	.069	.036	.074	.038	1.05	9	.127	.072	.128	.073	1.01
15	.104	.035	.111	.037	1.06	14	.200	.073	.200	.072	0.99
30	.197	.093	.222	.111	1.20	19	.272	.072	.275	.075	1.04
35	.227	.030	.261	.039	1.30	24	.343	.071	.362	.087	1.22
40	.260	.033	.306	.045	1.36	29	.415	.072	.458	.096	1.33
45	.295	.035	.353	.047	1.34	34	.490	.073	.560	.102	1.36
50	.327	.032	.399	.046	1.43	39	.565	.075	.667	.107	1.43
55	.357	.030	.445	.046	1.53	44	.638	.073	.771	.104	1.43
						49	.712	.074	.872	.101	1.37

catalyst so that the full rate of the reaction is not reached until the tube has been coated with carbon. The increase of the ratio of the off-gas to the entering gas is shown in Table VII. The data are given as taken from Runs 1, 3, 6 and 7. In the first column the elapsed time from the beginning of the run is given; in the second column, the total volume of the entering gas from the beginning of the run and in the fourth column the total volume of the off-gas from the beginning of the run. The figures in column three, *(a)*, represent the differences between successive figures in column two. Similarly, column five, (b), gives the differences between the readings in the fourth column. The ratio b/a, given in column six, represents the ratio of off-gas to entering gas over the period of time between successive readings of the wet-test meters which measured the entering and exit volumes. It is to be noted that these readings were not taken at regular intervals but this does not affect the ratios.

It can be seen readily that the ratios increase until a maximum is reached, and the maximum is reached in a shorter time at high temperatures than at low temperatures.

All the volumes in Table VII are expressed in cubic feet. The time is in minutes.

Summary

Propylene is rapidly decomposed at temperatures above 600° in pyrex or quartz. The gaseous products are largely hydrogen, methane and ethylene with smaller amounts of acetylene and ethane. Aromatic liquids (benzene, toluene, etc.), comprise approximately 25% of the total reaction products. The reaction has been shown to be predominantly homogeneous and unimolecular. A mechanism for the reaction is suggested.

Under comparable conditions in monel metal, decomposition of propylene begins at a much lower temperature, namely, 350°. The products are largely carbon and hydrogen and the reaction is autocatalytic.

As compared with isobutylene, propylene has been shown to undergo an almost identical type of pyrolysis.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

CARBITHIOIC ACID STUDIES.
II. CYCLOHEXYLCARBITHIOIC ACID AND VARIOUS DERIVATIVES

BY R. W. BOST AND W. W. WILLIAMS

RECEIVED SEPTEMBER 10, 1930 PUBLISHED DECEMBER 18, 1930

A number of carbithioic acids have been reported; however, the chemistry of these compounds seems to have been neglected. Recently Bost and Mattox[1] studied tolyl-4-carbithioic acid and found that the –CSSH group showed a striking resemblance to the –COOH group in some cases, while in others a great dissimilarity was noted.

In view of the fragmentary knowledge of the reactions of the –CSSH group, and of carbithioic acids in general, work has been extended to a new acid, cyclohexylcarbithioic acid. Its synthesis, its chemical and physical propetties, and certain derivatives are described.

Cyclohexylcarbithioic acid resembles its oxygen analog in the formation of salts, esters and toluides. It yields neither an acid chloride nor a thioamide. Oxidizing agents convert it into hexahydrobenzoic acid. The thioacyl peroxide was not obtainable.

Experimental Part

Cyclohexylcarbithioic Acid.—The Grignard reagent was made in the usual way from 0.5 mole of cyclohexyl bromide and 12.2 g. of magnesium. To this was added **38.1** g. of carbon disulfide and the method adopted by Bost and Mattox[1] in the preparation of tolyl-4-carbithioic acid followed, both in the preparation of the acid and in its purification.

Cyclohexylcarbithioic acid is a reddish-brown liquid with a putrid odor, and slowly decomposes on exposure to air. It distils with decomposition. It is soluble in most of the organic solvents. The acid is rather stable in ether solution. All its salts are stable. The sodium salt was used in the preparation of most of the derivatives.

Silver Salt of Cyclohexylcarbithioic Acid.—A saturated solution of silver acetate was added slowly, with stirring, to an ether solution of the acid until precipitation was complete. The precipitate was filtered, washed with water, alcohol and toluene, and dried. It is slightly soluble in hot alcohol and toluene.

Preparation of Esters.—The methyl and ethyl esters were made from the sodium salt of the acid and the corresponding alkyl sulfates. The propyl and butyl esters were made by refluxing equivalent quantities of the sodium salt and the corresponding alkyl bromides. The esters were purified by the usual method.

p-Toluide of Cyclohexylcarbithioic Acid.—Ten grams of *p*-toluidine, 6 g. of the dry sodium salt and 6 ml. of concentrated hydrochloric acid were heated to gentle boiling in a beaker for thirty minutes. The mass was extracted with 50 ml. of hot toluene, boiled with charcoal, filtered and allowed to crystallize. The toluide separated in large colorless needles. It is soluble in hot alcohol, toluene and benzene.

Attempt to Prepare the **Thioamide.**—The method adopted by Bost and Mattox[1]

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[1] Bost and Mattox, THIS JOURNAL, 52,332 (1930).

in the preparation of the amide of tolyl-4-carbithioic acid was used. After a few days a solid separated. It consisted of white glistening leaflets melting at 185–187°. The product contained nitrogen but no sulfur. Further investigation showed the substance to be the amide of hexahydrobenzoic acid.

Action of Oxidizing Agents.—To an ether solution of the acid at room temperature was added concentrated nitric acid with stirring until the color was discharged. After several hours the product was extracted with ether and purified through its sodium salt. It melted at 28° and gave negative tests for sulfur. Other tests showed the substance to be hexahydrobenzoic acid.

TABLE I

DATA ON DERIVATIVES

Compound	Color	Solvent	M. p. or b. p., °C
1 Silver salt	Brick-red	Insoluble	163
2 *p*-Toluide	Colorless	Alcohol	160
3 Methyl ester	Orange-red	....	90 (3 mm.)
4 Ethyl ester	Orange-red	....	106 (5 mm.)
5 n-Propyl ester	Orange-red	....	106 (3 mm.)
6 n-Butyl ester	Orange-red	....	145 (5 mm.)

TABLE II

ANALYSES

Formula	Sulfur, % Calcd.	Sulfur, % Found	Silver, % Calcd.	Silver, % Found
1 $C_7H_{11}S_2Ag$	24.01	23.99	40.39	40 31
2 $C_{14}H_{19}NS$	13.75	13.87		
3 $C_8H_{14}S_2$	36.80	36.69		
4 $C_9H_{16}S_2$	34.06	34.12		
5 $C_{10}H_{18}S_2$	31.70	31.80		
6 $C_{11}H_{20}S_2$	29.65	29.75		

Summary

1. A new carbithioic acid has been prepared and its properties described.
2. The acid readily forms salts, esters and toluides.
3. Attempts to prepare the acid chloride and thioamide met with failure.

CHAPEL HILL, NORTH CAROLINA

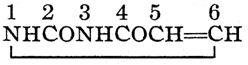
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON PYRIMIDINES. CXIX. DETERMINATION OF THE CONSTITUTION OF ALKYLATION PRODUCTS OF PHENYLURACIL AND PHENYLHYDROURACIL[1]

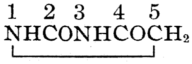
BY JANET EVANS AND TREAT B. JOHNSON

RECEIVED SEPTEMBER 17, 1930 PUBLISHED DECEMBER 18, 1930

In uracil, as in hydantoin, the hydrogen atoms attached to each nitrogen atom can be replaced with alkyl or substituted alkyl groups by appropriate methods. If only one group is substituted, it enters the hydantoin molecule in the 3-position.[2] This is not always true of the pyrimidine series, mixtures of N-1 and N-3 substitution products being formed in some cases.[3,4] The position of the entering group in hydantoin can be determined directly by identifying the a-amino acids formed when the molecule undergoes complete hydrolysis.[2] On the other hand, the double bond of uracil is not easy to reduce,[5] and hydrouracils are hydrolyzed either only partially with the formation of the ureido acids, or are broken down completely, probably because the β-amino acids which would be formed are more unstable[6] than the a-amino acids which result from the hydrolysis of hydantoins. The present investigation was undertaken with a view to establish some method for the determination of the position of an entering group.


$\underbrace{\overset{1}{\mathrm{N}}\mathrm{H}\overset{2}{\mathrm{C}}\mathrm{O}\overset{3}{\mathrm{N}}\mathrm{H}\overset{4}{\mathrm{C}}\mathrm{O}\overset{5}{\mathrm{C}}\mathrm{H}{=}\overset{6}{\mathrm{C}}\mathrm{H}}$

Uracil


$\underbrace{\overset{1}{\mathrm{N}}\mathrm{H}\overset{2}{\mathrm{C}}\mathrm{O}\overset{3}{\mathrm{N}}\mathrm{H}\overset{4}{\mathrm{C}}\mathrm{O}\overset{5}{\mathrm{C}}\mathrm{H}_2}$

Hydantoin

Since uracil and hydantoin are somewhat related and since comparison of the ultraviolet absorption spectra of hydantoin compounds had proved useful in the identification of substituted hydantoins,[7,8] it seemed advisable to prepare a series of substituted uracils and to study their spectra in the ultraviolet. Uracils isomeric with hydantoins, whose spectra[8] had been determined, were chosen so that structural differences between uracils and hydantoins could also be studied. The absorption spectra will be published in a later paper.

Another consideration which led to the choice of this series of uracil

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[1] Constructed from a dissertation presented by Janet Evans to the Faculty of the Graduate School of Yale University in June, 1929, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Johnson and Bates, THIS JOURNAL, 38, 1087 (1916).

[3] Johnson and Hahn, *ibid.*, 39, 1256 (1917).

[4] Behrend and Dietrich, *Ann.*, 309, 265 (1899).

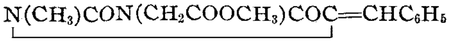
[5] Behrend, *ibid.*, 229, 38 (1885); 251, 239 (1899).

[6] Rodionow, THIS JOURNAL, 51, 850 (1929).

[7] Carr and Dobbrow, *ibid.*, 47, 2961 (1925); Carr, Report at Richmond Meeting of the American Chemical Society, April, 1927; Maclean, Thesis, Mount Holyoke College, 1926.

[8] Hahn and Evans, THIS JOURNAL, 50, 806 (1928).

compounds for synthesis was the fact that in the course of the synthesis of methyl N-1-methyl-5-benzalhydantoin-N-3-acetate[9]



$$\underbrace{N(CH_3)CON(CH_2COOCH_3)COC}=CHC_6H_5$$

it was noted that the two isomeric esters of this constitution (m. p. 66" and 98°) suffer a transformation to the same compound (m. p. 278°) when they are allowed to stand in the light. This new compound is extremely insoluble as well as high melting, and its analysis showed it to have the same empirical formula as the esters from which it was obtained. The acid corresponding to the esters and melting at 198–199.5° was similarly transformed by light to an insoluble substance at 310°.

At the time the possibility of a rearrangement from a five- to a six-membered ring with the formation of the isomeric substituted uracil was considered.[9] Synthesis of the pyrimidine to which the ester and acid might rearrange and comparison of their properties with those of the compounds melting at 278 and 310° would definitely prove whether a change in the number of atoms in the ring had taken place.

The present experimental evidence can lead us to no such conclusions. The uracil derivative, methyl N-1-methyl-6-phenyl-uracil-N-3-acetate, VI (see chart), has properties differing widely from those of the product formed by the action of light on the isomeric hydantoin. The former has a melting point of 159° and is very soluble in alcohol, whereas the latter melts at 278°, and is practically insoluble. The corresponding acid melts at 261°, in contrast to 310°, and is moderately soluble in alcohol. No evidence of the true structure of the compounds melting at 278 and 310° has as yet been obtained.

The compound methyl N-1-methyl-6-phenyl-uracil-N-3-acetate, VI, was synthesized by three different series of transformations, one of which definitely proves its structure. The course of the transformations and other minor relationships can be visualized by reference to the chart. The methods will be discussed separately.

In carrying out the first series, it was found that alkylation of 6-phenyluracil, with either methyl iodide or ethyl chloro-acetate, resulted in the formation of but one monosubstitution product, numbered, respectively, I and III. Another product was isolated from the treatment with methyl iodide, and was proved to be dimethyl-6-phenyluracil, II. That the positive methyl group and the less positive ethyl acetate residue enter the same position in the ring is proved by the following facts.

The methyl derivative, I, prepared by the alkylation of 6-phenyluracil has very different properties from those of the I-methyl-6-phenyluracil, XVIII, synthesized from benzalmethylamine. The former crystallizes in glistening leaves and melts at 228–230°, whereas the latter occurs in long

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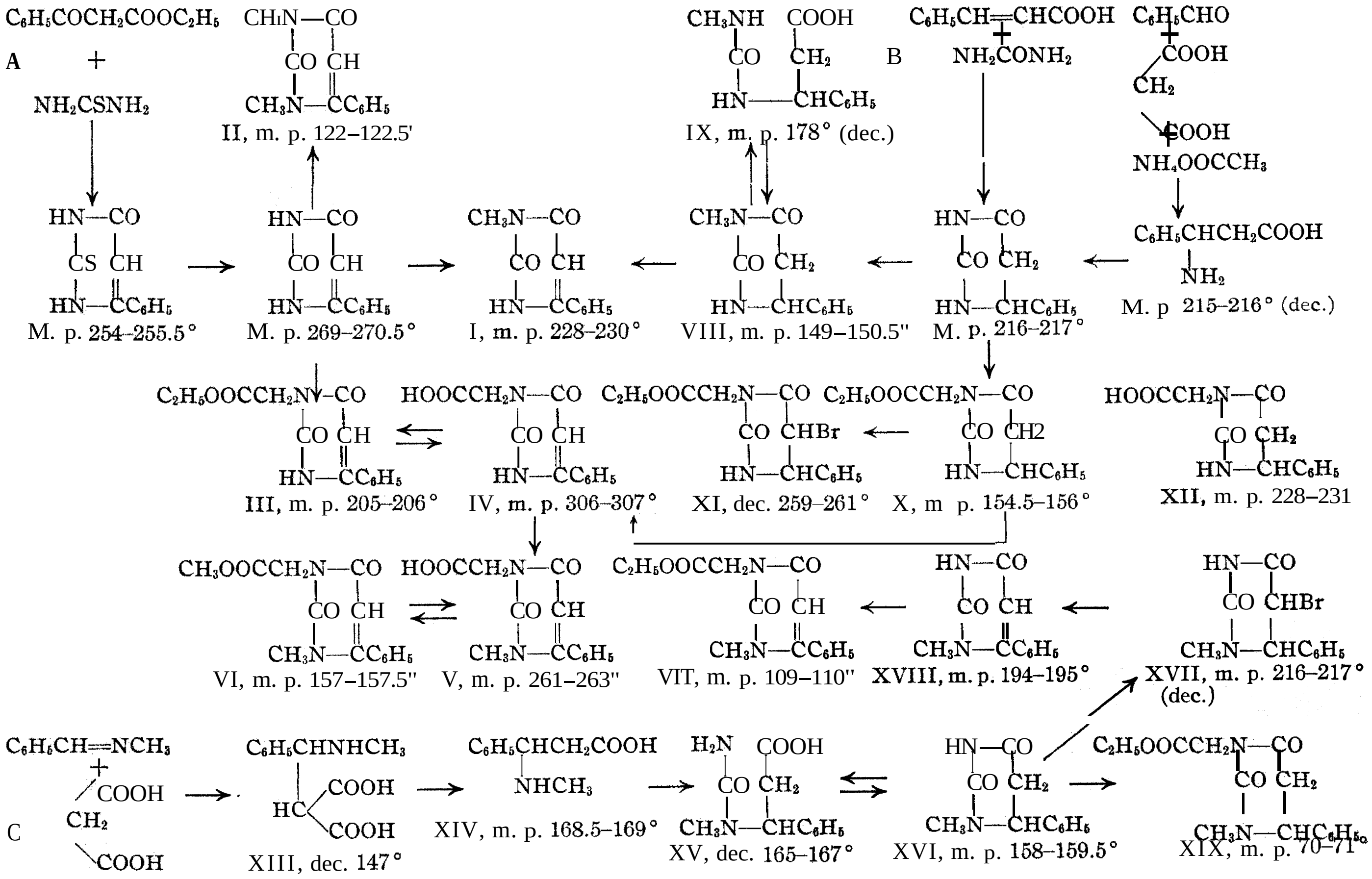
[9] Hahn and Evans, THIS JOURNAL, 49,2877 (1927).


A
B
C
II, m. p. 122–122.5°
IX, m. p. 178° (dec.)
M. p. 254–255.5°
M. p. 269–270.5°
I, m. p. 228–230°
VIII, m. p. 149–150.5°
M. p. 216–217°
M. p. 215–216° (dec.)
III, m. p. 205–206°
IV, m. p. 306–307°
XI, dec. 259–261°
X, m. p. 154.5–156°
XII, m. p. 228–231
VI, m. p. 157–157.5°
V, m. p. 261–263°
VII, m. p. 109–110°
XVIII, m. p. 194–195°
XVII, m. p. 216–217° (dec.)
XIII, dec. 147°
XIV, m. p. 168.5–169°
XV, dec. 165–167°
XVI, m. p. 158–159.5°
XIX, m. p. 70–71°

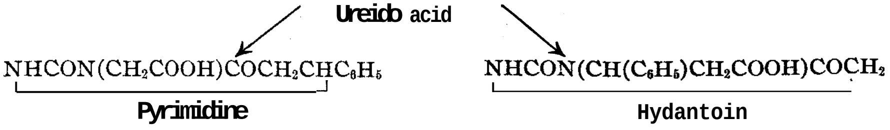
slender needles and melts at 194–195°. The nitrogen content of the two compounds is identical. Since the method of preparation of the latter substance requires that the methyl group must be in the 1-position, it follows that the hydrogen in the 3-position of the former compound must have been replaced by a methyl group.

Similarly, the methyl derivative, V, of ethyl 6-phenyl-uracil-N-3-acetate, III, which was prepared by alkylation of the corresponding acid, IV, with dimethyl sulfate and subsequent esterification, was shown by mixed melting point determinations and analyses to be the same compound as that prepared from 1-methyl-6-phenyluracil, XVIII, by treatment with ethyl chloro-acetate. On saponification, a sample of the ester formed from 1-methyl-6-phenyluracil was transformed into the corresponding acid, which has the same properties as those of the acid prepared by methylation of the 6-phenyl-3-acetic acid, IV. Thus the acetic acid or ester residue is in the 3-position, which is the same position entered by the methyl group.

The yield of substituted 6-phenyl-uracils was very low; moreover, it was found that reduction to the corresponding saturated compounds could not be effected by ordinary means. The saturated compounds were therefore prepared by alkylation of phenyl-hydrouracil. Their relationships to the unsaturated compounds were demonstrated by the substitution of bromine in position 5 of the ring,[10] and subsequent expulsion of hydrogen bromide. The products were identical with those prepared by alkylation of phenyluracil.

The hydrolysis of these saturated compounds cannot be used to determine their constitution. It was found that 3-methyl-6-phenyl-5,6-dihydrouracil VIII is rather readily hydrolyzed to the corresponding ureido acid IX, but prolonged action of boiling barium hydroxide solution at atmospheric pressure failed to complete the hydrolysis. When the compound was heated with barium hydroxide solution in a sealed tube at 150°, complete destruction of the molecule resulted.

Alkylation of 6-phenyl-5,6-dihydrouracil with ethyl chloro-acetate resulted in the formation of a mixture of which the major portion was identified as ethyl-6-phenyl-5,6-dihydrouracil-N-3-acetate. Two acids were obtained by the saponification of this ester in either acid or alkaline solution. Of these, the one, XII, melting at 231°, is that related to the original ester since it reverts to that ester on treatment with absolute alcohol and dry hydrogen chloride. The formation of the other acid may be accounted for by the following mechanism



$$\mathrm{HOOCCH_2NHCONHCH(C_6H_5)CH_2COOH}$$

$$\mathrm{\underline{NHCON(CH_2COOH)COCH_2CHC_6H_5}} \qquad \mathrm{\underline{NHCON(CH(C_6H_5)CH_2COOH)COCH_2}}$$

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[10] Fischer and Roeder, *Ber.*, **34**, 3763 (1901).

Hydrouracils can be hydrolyzed to the corresponding ureido acids, and reclosure of the ring effected by heating in acid solution. Two possibilities for ring formation from the ureido acid in question are evident. The validity of this explanation has not been determined.

The synthesis of N-1-methyl-6-phenyl-5,6-dihydrouracil, XVI, which now became essential for the proof of the structure of the whole series, depends on the fact that β-amino acids react with potassium cyanate[11] in water solution and then undergo rearrangement to *β-ureido* **acids,** which form hydrouracils on the closure of the ring. Accordingly the acid β-N-methylamino-β-phenylpropionic acid, XIV, had to be synthesized.

A modification of the recent method of Rodionow for the synthesis of β-amino acids[12] seemed the most promising for the synthesis of β-N-methyl-β-phenylpropionic acid, especially since it offered a plausible mechanism of his reaction. Rodionow discovered that the reaction of alcoholic solutions of ammonia or amines with aldehydes and malonic acid is more complicated than Knoevenagel[13] supposed and results in the formation of β-amino acids as well as cinnamic acids.

The repetition of Knoevenagel's experiments with acid and neutral ammonium malonate and benzaldehyde in the present investigation shows that besides the cinnamic acid, which was formed in slightly smaller amounts than those reported by him, the corresponding 8-amino acid was isolated in yields corresponding to slightly more than 50% of the calculated amount. Ammonium acetate was also used very successfully as a source of ammonia with benzaldehyde and malonic acid in alcoholic solution.

The reaction of malonic acid with benzalmethylamine, the aliphatic analog of Knoevenagel's benzalaniline, proceeds to form β-methylamino-β-phenylpropionic acid, XIV, and cinnamic acid in approximately equal amounts. The intermediate addition product, XIII, of benzalmethylamine and malonic acid was isolated in pure condition. On heating, it undergoes decomposition, giving a mixture of 8-amino acid and cinnamic acid.

The isolation of this amine dicarboxylic acid addition product offers some positive evidence in support of Rodionow's postulation[14] that the formation of β-amino acids from an aldehyde, ammonia and malonic acid proceeds in the following order: first, condensation of aldehyde and ammonia to form an imine; second, addition of malonic acid to the double bond; and, finally, loss of carbon dioxide. This mechanism is the most plausible one suggested. The relative yields of β-amino acid and cinnamic acid depend on the stability of the former.

N-1-methyl-6-phenyl-dihydrouracil, XV, was formed without difficulty

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[11] Lengfeld and Stieglitz, Am. Chem. J., 15, 516 (1893).

[12] Rodionow and Malewinskaja, Ber., 59, 2952 (1926).

[13] Knoevenagel, *ibid.*, 31, 2596 (1898).

[14] Rodionow and Postovskaja, THIS JOURNAL, 51, 841 (1929).

from the β-amino acid by the use of potassium cyanate in neutral solution and could be made to condense quantitatively with ethyl chloro-acetate in the presence of sodium ethylate to form the disubstituted saturated uracil, XIX.

N-1-methyl-6-phenyl-hydrouracil, XVI, is converted quantitatively by the action of bromine in chloroform solution under pressure into the 5-bromine substitution product, XVII, which loses hydrogen bromide on heating at its decomposition point and forms the theoretical amount of 1-methyl-6-phenyluracil, XVIII. Condensation of the latter compound with ethyl chloro-acetate in the presence of sodium ethylate results in nearly quantitative formation of ethyl N-1-methyl-6-phenyl-uracil-1-acetate, VII. Saponification of the ester obtained by this method results in the formation of the acid V. Both acid and ester are identical in properties with the products obtained by direct substitution of phenyluracil.

The synthesis from benzalmethylamine in addition to its inherent theoretical interest, and its being absolute proof of the structure of the disubstituted uracils, was also the most efficient method for their preparation, since the yields of each of the intermediate products were extremely good.

Experimental Part

A. Derivatives of 6-Phenyluracil

The 6-phenyluracil, used as a starting point in this investigation was prepared according to the method of Johnson and Hemingway.[15] This method involves the condensation of ethyl benzoylacetate[16] and thiourea to form 6-phenyl-2-thiouracil and the subsequent desulfurization of this compound. The 6-phenyluracil obtained in this way was recrystallized once before using for syntheses.

N-3-methyl-6-phenyluracil, I, (m. p. 228–230°), and **N-1-3-dimethyl-6-phenyluracil, II,** (m. p. 122–122.5°) were prepared simultaneously by treating 6-phenyluracil with methyl iodide in alkaline solution.

The general method is illustrated by the following experiment. Ten grams of 6-phenyluracil (m. p. 269–270 5°) was refluxed on the steam-bath for six hours with a solution of 1.2 g. of sodium in 100 cc. of methyl alcohol. Excess methyl iodide was added and refluxing continued for twenty-four hours or until the sodium salt had disappeared and the solution had become neutral. On evaporation, 5 g. of material melting from 110 to 210° and 4 g. melting from 89 to 125° were obtained. Since it was found that the substituted uracils are much more soluble in boiling chloroform than the unsubstituted phenyluracil, separation of these mixtures could be accomplished with comparative ease. Extraction of these two successive precipitates with boiling chloroform gave in the first case, 2 g. of almost pure mono-methyluracil (m. p. 225–228°); and in the second case, 3 g of dimethyluracil, m. p. 106–118°. The combined residues, insoluble in chloroform, amounted to 4 g. of unsubstituted phenyluracil fm. p. 265–269°). Evaporation of the mother liquor gave products contaminated with iodine and which could not be further purified. Iodoform separated in several cases and was identified by mixed melting point determinations. Only one monomethyl derivative was ever isolated from the reaction mixture although diligent search was made for another.

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[15] Johnson and Hemingway, THIS JOURNAL, 37,379 (1915).

[16] Wahl and Doll, Bull. *soc. chim.*, [4]13,265 (1913).

N-3-methyl-6-phenyluracil, I, m. p. 228–230°, was also prepared by treating N-3-methyl-6-phenyl-5,6-dihydrouracil, VIII, with bromine. Equal molecular quantities of bromine and hydrouracil were heated for one hour in a sealed tube with acetic acid as a solvent. Half of the product consisted of N-3-methyl-6-phenyluracil, m. p. 224–229°, which does not lower the melting point of the product obtained by direct methylation of phenyluracil. The rest of the product was a mixture, m. p. 140–155°, which contained the original N-3-methyl-6-phenyl-dihydrouracil.

After four recrystallizations from boiling alcohol, its melting point remained constant at 228–230°. It is soluble in boiling alcohol and precipitates in the form of large glistening leaves. It is also soluble in boiling chloroform.

Anal. Calcd. for $C_{11}H_{10}O_2N_2$: N, 13.86. Found: N, 13.80, 13.75.

N-1-3-dimethyl-6-phenyluracil, II, m. p. 122–122.5°, is soluble in chloroform and in boiling alcohol. After four recrystallizations from alcohol, from which it precipitates as small glistening leaves, a sample melting at 122–122.5° was used for analysis.

Anal. Calcd. for $C_{12}H_{12}O_2N_2$: N, 12.96. Found: N, 13.01, 13.17.

Potassium 6-phenyluracil was prepared by boiling 15 g. of 6-phenyluracil with a solution of one equivalent of potassium hydroxide in 150 cc. of water and filtering out the undissolved uracil. Its melting point lies above 300°. After one recrystallization from boiling water the salt was analyzed.

Anal. Calcd. for $C_{10}H_8O_2N_2K$: N, 12.33. Found: N. 12.61, 12.63.

Ethyl-6-phenyluracil-N-3-acetate, III, m. p. 205–206°, was prepared from 6-phenyluracil by treatment with sodium ethylate and ethyl chloro-acetate. In a sample experiment, 25 g. of 6-phenyluracil was refluxed for three-quarters of an hour with a solution of 4 g. of sodium in 300 cc. of absolute alcohol. Twenty-five grams of ethyl chloroacetate was added and the refluxing continued until the solution was practically neutral, which required ten days. Nearly complete precipitation was brought about by the addition of an equal volume of water and a few drops of hydrochloric acid. Boiling chloroform extracted 4.3 g. of ester from this precipitate, leaving 19 g. of unchanged phenyluracil. Although the ester was prepared several times with variations in the length of time of heating, no better yields were obtained. No evidence of the formation of the isomeric N-1 substituted compound was obtained. When two equivalents of sodium was used with 35 g. of phenyluracil, the yield of ester was increased to 8 g., and 19.7 g. of phenyluracil was recovered unchanged. On long standing, additional precipitates were obtained from the mother liquor aggregating 7.6 g., m. p. 75–220°. This gave more ester on extraction with chloroform.

Anal. Calcd. for $C_{14}H_{14}O_4N_2$: N, 10.22. Found: N, 10.19, 10.42, 10.49.

The ester passes quantitatively into the salt of the corresponding acid IV, m. p. 305°, on saponification with potassium hydroxide. The ester is soluble in boiling alcohol from which it can be conveniently recrystallized. It forms as fine colorless needles.

6-Phenyluracil-N-3-acetic, IV, m. p. 304–305°, was obtained in quantitative yield by boiling the corresponding ester with about six equivalents of dilute potassium hydroxide for one and one-half hours and acidifying the resulting solution with hydrochloric acid. It is insoluble in water and only very slightly soluble in boiling alcohol and acetone. It can be recrystallized most conveniently irom boiling glacial acetic acid, in the form of tiny clear cubes.

Anal. Calcd for $C_{12}H_{10}O_4N_2$: N, 11.39. Found: N, 11.12, 11.27.

The acid can be esterified by treatment of its suspension in absolute alcohol with dry hydrogen chloride, when it passes quantitatively to the ester, III, m. p. 205–206°. When treated with dimethyl sulfate it yields the N-1-methyl derivative, V. The acid is also formed when ethyl 6-phenyl-5,6-dihydrouracil-3-acetate, X, is treated with bromine in a sealed tube.

N-1-methyl-6-phenyluracil-N-3-acetic acid, V, m. p. 261–263°, was readily prepared by treating **6-phenyluracil-N-3-acetic** acid, IV, with dimethyl sulfate. For example, 7 g. of acid, m. p. 303–305°, was dissolved in a solution of somewhat more than two equivalents of potassium hydroxide in 100 cc. of alcohol. About 9 moles of dimethyl sulfate (15 cc.) was added dropwise and alternately with a solution of potassium hydroxide to keep the reaction mixture alkaline. The mixture was refluxed for half an hour to destroy any excess dimethyl sulfate, evaporated to small volume, diluted with water and acidified with hydrochloric acid. An immediate precipitate of 7.3 g. of an acid resulted.

Anal. Calcd. for $C_{13}H_{12}O_4N_2$: N, 10.77. Found: N, 10.63, 10.67.

The acid is very slightly soluble in boiling water, but it is soluble in boiling glacial acetic acid and in boiling ethyl alcohol, from which it crystallizes in the form of small clear cubical crystals.

Methyl-N-1-methyl-6-phenyluracil-N-3-acetate, VI, m. p. 157–157.5°, was formed quantitatively by alternately saturating with hydrogen chloride and refluxing a suspension of the corresponding acid, V, in methyl alcohol.

Anal. Calcd. for $C_{14}H_{14}O_4N_2$: N, 10.21. Found: N, 10.06, 10.21.

The ester is very soluble in boiling alcohol, but is much less soluble in cold alcohol. It crystallizes in stout colorless needles. On saponification with concentrated hydrochloric acid the ester reverts quantitatively to the acid V.

Ethyl-N-1-methyl-6-phenyluracil-N-3-acetate, VII, m. p. 109–110, was prepared from the acid, V, by the above method using absolute ethyl alcohol in place of methyl alcohol. The yield was quantitative, 2.9 g. of ester resulting from the esterification of 2.6 g. of acid. Its analysis is given below (a). This ester was also prepared by treating 2.8 g. of N-1-methyl-6-phenyluracil, XVIII, with 0.4 g. of sodium in 40 cc. of absolute alcohol, and 0.8 g. of ethyl chloro-acetate. The sodium salt, which precipitated immediately on the addition of the uracil to the sodium ethylate solution, was refluxed for fifteen minutes before the addition of the ethyl chloro-acetate, and refluxing continued for four hours thereafter, or until the solution had become neutral to litmus. Water was added causing successive precipitates which aggregated 3.1 g. of fairly pure ester. After four recrystallizations it was analyzed (b).

Anal. Calcd. for $C_{15}H_{16}O_4N_2$: N, 9.72. Found: (a) N, 9.85, (b) N, 9.98.

The ester is very soluble in boiling alcohol and in 50% alcohol, from which it crystallizes in clusters of long, very fine silky needles. On saponification with concentrated hydrochloric acid it passes quantitatively into the corresponding acid, V.

Reduction of N-1-methyl-6-phenyl-N-3-acetic acid or its methyl ester could not he accomplished by catalytic methods, nor by the use of hydrogen iodide, both of which had proved successful in reducing the isomeric hydantoins.[8] Units of 1.5 g. of acid or ester were used and recovered quantitatively in each of the four experiments. In two cases, one with the acid and one with the ester, hydrogen was used with colloidal palladium as a catalyst.[17] In the third the acid was heated for two hours at 120–130" with 5 cc. of hydrogen iodide, 0.5 g. of red phosphorus and 20 cc. of acetic acid. In the fourth, the acid was heated for five hours at 140–145° with 1.0 g. of red phosphorus and 30 cc. of hydrogen iodide, sp. gr. 1.70.

B. Derivatives of 6-Phenyl-5,6-dihydrouracil

6-Phenyl-5,6-dihydrouracil was prepared by heating cinnamic acid with urea, the general method of Fischer and Roeder.[10] Their procedure was modified by decreasing

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[17] Hahn and Gilman, THIS JOURNAL, 47, 2948 (1925).

the temperature from 250 to 190°, and increasing the length of time of heating from one to six hours, whereby the yields were nearly tripled. From 50 g. of cinnamic acid and 30 g. of urea yields of 22–24 g. of phenyldihydrouracil, m. p. 215–217°, were obtained. This melting point agrees with that given by Posner[18] and by Dakin,[19] 216–217°, rather than that obtained by Fischer,[10] 202–203°.

6-Phenyl-5,6-dihydrouracil was also prepared by treating a solution of β-phenyl-β-aminopropionic acid with potassium cyanate and evaporating to dryness.'' The product was dissolved in a little water and acidified with hydrochloric acid. The precipitate, m. p. 183–186°, proved to be the ureido acid and passed quantitatively into phenyl-hydrouracil (m. p. 215–217°) on heating with 10% hydrochloric acid. Mixed melting point determinations demonstrated the identity of these compounds with those obtained by Fischer's synthesis.

The β-phenyl-β-aminopropionic acid used in the above synthesis was prepared by treatment of 3 g. of benzaldehyde with 3 g. of malonic acid, 4.5 g. of ammonium acetate and 25 cc. of absolute alcohol. The materials were refluxed for two hours, during which time carbon dioxide was evolved. On coding, 3.2 g. of amino acid decomposing at 213–215° precipitated, and from the filtrates, 1.2 g. of cinnamic acid, m. p. 128–131°.

In several experiments ammonium malonate was used in place of malonic acid and ammonium acetate. The ammonium malonate was prepared by treating a solution of malonic acid in dry ether with a stream of dry ammonia gas.[20]

From 10 g. of the mono-ammonium malonate refluxed for two hours with 10 g. of benzaldehyde and 25 cc. of absolute alcohol, 6 g. of amino acid and 3.2 g. of cinnamic acid were obtained; from 6 g. of the mixture of mono and di-ammonium malonate refluxed for three and one-half hours with 4.6 g. of benzaldehyde and 25 cc. of absolute alcohol, 3.2 g. of amino acid and 2.8 g. of cinnamic acid were obtained. After recrystallization from boiling alcohol, the amino acid melted at 215–216°. Since the melting point does not agree with that given by Posner,[18] 231°, or Rodionow,[12] 228°, the identity of the compound was established by an analysis.

Anal. Calcd. for $C_9H_{11}O_2N$: N, 8.49. Found: N, 8.48.

N-3-methyl-6-phenyl-5,6-dihydrouracil, VIII, m. p. 149–150.5°, was prepared by the following method. The sodium salt of 6-phenyl-5,6-dihydrouracil was formed by refluxing 17.5 g. of the hydrouracil with a solution of 2.3 g. of sodium in 300 cc. of absolute alcohol for one hour. The addition of 20 g. of methyl iodide caused almost immediate solution of the salt. Refluxing was continued for one-half hour. On standing for twenty-four hours and further evaporation, 14 g., m. p. 145–149°, precipitated and a small amount of unchanged hydrouracil was recovered. The methylated compound was purified by recrystallization from boiling water and alcohol, from which it precipitates in the form of needles.

Anal. Calcd. for $C_{11}H_{12}O_2N_2$: N, 13.73. Found: N, 13.88, 13.86.

On treatment with bromine, in sealed tubes, N-3-methyl-6-phenyl-5,6-dihydrouracil can be transformed into the corresponding unsaturated compound, I. On hydrolysis at atmospheric pressure the corresponding ureido acid IX is formed.

Hydrolysis of N-3-methyl-6-phenyl-5,6-dihydrouracil, VIII.—The hydrolysis was conducted both at atmospheric pressure and at elevated pressures. In the first case, 6.4 g. of hydrouracil was digested with 50 g. of barium hydroxide, 100 cc. of water and 100 cc. of methyl alcohol for one hundred hours. After removing the solid barium

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[18] Posner, Ber., 38, 2316 (1905).

[19] Dakin, J. Biol. Chem., 8, 39 (1910).

[20] McMaster, Am. Chem. J., 49, 295 (1913).

hydroxide by filtration, the solution was distilled into weak hydrochloric acid. A very small amount of methylamine hydrochloride contaminated with ammonium chloride was isolated from the distillate. The residue in the flask was exactly neutralized with sulfuric acid and filtered from the barium sulfate. A precipitate of 2.6 g. of coarse needles which decompose at 178° resulted after further evaporation. This compound reverted quantitatively to the original hydrouracil on treatment with 10% hydrochloric acid. This result and the following analysis of the product decomposing at 178° established the fact that the hydrouracil is hydrolyzed with the formation of the ureido acid IX, on prolonged treatment with barium hydroxide and that complete hydrolysis cannot be effected by this means.

Anal. Calcd. for $C_{11}H_{14}O_3N_2$: N, 12.61. Found: N, 12.70, 12.74.

The molecule degenerated completely when N-3-methyl-6-phenyl-5,6-dihydrouracil (3.5 g.) was heated at 150° for seventy-two hours in a sealed tube with excess barium hydroxide and a little water and subsequently treated as described above. The acid distillate yielded 1.5 g. of solid which was extracted with absolute butyl alcohol and found to consist of nearly the theoretical quantities of ammonium chloride and methylamine hydrochloride. After the barium had been removed from the reaction mixture and the filtrate evaporated to dryness only 0.5 g. of a substance, m. p. 115–120°, remained. This was found to be neither benzoic acid nor cinnamic acid. The peculiar odor and lachrymal effect of the vapors indicate that the other products of this profound decomposition are volatile with steam. It is evident that this method cannot be used for the determination of the position of the methyl group.

Ethyl-6-phenyl-5,6-dihydrouracil-N-3-acetate, X, m. p. 154.5–156°, is the major product formed when the sodium salt of phenyl-dihydrouracil is treated with ethyl chloro-acetate. Twenty grams of phenyl-dihydrouracil was refluxed for four hours with two equivalents of sodium (4.8 g.) in 250 cc. of absolute alcohol; 40 g. of ethyl chloro-acetate was added and refluxing continued for nine hours or until the solution was neutral. The addition of an equal volume of water caused the precipitation of 10.4 g., m. p. 135–170°. The filtrate was evaporated to dryness and extracted with chloroform and then alcohol. From the chloroform solution 2.7 g. of a mixture, m. p. 110–128°, was obtained. This mixture was never resolved, though several attempts with chloroform, water and alcohol were made. The alcohol extraction yielded 3,4 g. of original hydrouracil. The ester was obtained by extraction of the first precipitate with chloroform, leaving a residue of 1.7 g. of the original hydrouracil. The extract was recrystallized from boiling alcohol, giving 5.1 g., m. p. 148–151°. After several recrystallizations from boiling alcohol, from which it precipitates as fine white needles, its melting point remained constant at 154.5–156°.

Anal. Calcd. for $C_{14}H_{16}O_4N_2$: N, 10.15. Found: N, 10.15, 10.17.

On hydrolysis the ester is converted into a mixture from which the acid, XI, m. p. 228–231°, can be isolated. Treatment with bromine also results in the formation of a mixture from which a bromine compound, XII, and the corresponding unsaturated acid, IV, were isolated.

Bromination of **ethyl-6-phenyl-5,6-dihydrouracil-N-3-acetate** was carried out at 100° in a sealed tube. Three grams of the hydrouracil was heated with 1.5 moles of bromine in glacial acetic acid for three hours. After neutralization, a precipitate of 2.8 g. which decomposed at 212–235° was obtained. This was recrystallized from boiling alcohol, giving 0.8 g. of a bromine compound, XI, which forms in spongy balls and melts at 259–261° with decomposition.

Anal. Calcd for $C_{14}H_{15}O_4N_2Br$: N, 7.89. Found: N, 7.61, 7.63.

From the filtrate, 0.35 g. of original ester and 1.3 g. of a mixture melting from 80° to above 267° were obtained.

In a second experiment the heating at 100° was continued for seven hours and resulted in the formation of another mixture. In this case, however, no pure bromine compound could be isolated but a small amount (0.8 g.) of material melting at 350° was obtained by recrystallization. It was proved to be 6-phenyluracil-N-3-acetic acid, IV, by a mixed melting point determination. The remainder of the material consisted of a mixture melting from 180 to 275" with decomposition. Although this method is not feasible for the preparation of the acid, IV, the relationship between the two compounds has been definitely established.

6-Phenyl-5,6-dihydrouracil-N-3-acetic acid, XII, m. p. 228–231°, can be isolated from the mixture formed when the corresponding ester, X, is hydrolyzed in either acid or alkaline solution. The proportion of it is practically the same in either case. When 0.5 g. of pure ester was boiled with 30 cc. of concentrated hydrochloric acid for two hours, 0.2 g., m. p. 228–231°, and 0.2 g., m. p. 165–215°, were obtained. The product melting at 228–231° passed quantitatively to the ester, m. p. 154.5–156°, on treatment with absolute ethyl alcohol and dry hydrogen chloride. On esterification of the mixture, both the original ester, m. p. 148–152°, and a new ester, m. p. 132–135°, were obtained. This latter ester was not obtained in large enough quantities for analysis.

When 5 g. of ester, m. p. 154.5–156°, was refluxed with potassium hydroxide for one and one-half hours and the resulting solution acidified, 4.2 g., m. p. 180–220°, precipitated. This was resolved into two products, 2.6 g., m. p. 228–231°, and 1.0 g., m. p. 170–180°, by one recrystallization from boiling alcohol. Further recrystallization from boiling alcohol failed to alter the melting point.

Anal. Calcd. for $C_{12}H_{12}O_4N_2$: N, 11.29. Found: N, 11.07, 11.19.

C. Derivatives of Benzalmethylamine

β-N-methyl-benzylmalonic acid, XIII, decomposition point 147°, is the primary product of the action of malonic acid on benzalmethylamine. It is formed with the evolution of heat and begins to precipitate from the reaction mixture almost immediately. On further heating it loses carbon dioxide to form the corresponding β-aminopropionic acid, XIV, and cinnamic acid. It was recrystallized once from boiling alcohol.

Anal. Calcd. for $C_{11}H_{13}O_4N$: N, 6.28. Found: N, 6.53.

β-N-methyl-β-phenylpropionic Acid, XIV, m. p. 168.5–169°.—Benzalmethylamine (20 g.), malonic acid (16.7 g.) and absolute alcohol (80 cc.) were mixed and warmed gently on the steam-bath. After five to ten minutes the solution was filled with the feathery white crystals of the malonic acid addition product and carbon dioxide was being given off. The refluxing was continued, causing the gradual disappearance of the precipitate. At the end of three hours solution was complete and evolution of carbon dioxide had ceased. The solution was cooled in a freezing mixture and the product precipitated slowly as a white powder by addition of ether or by seeding. The precipitate obtained by seeding always contained some cinnamic acid. The yield of β-amino acid was 12 g., and of cinnamic acid obtained from the ether solution, 9 g. Small amounts of benzaldehyde and benzoic acid were also detected.

Anal. Calcd. for $C_{10}H_{13}O_2N$: N, 7.82. Found: N, 7.72, 7.71.

The acid precipitates as feathery crystals from pure boiling alcohol, in which it is less soluble than it is in the reaction mixture. It is extremely soluble in hydrochloric acid. From the latter, the hydrochloride crystallizes in clusters of needles.

β-Phenyl-β-N-1-methyl-ureido-propionic acid, XV, m. p. 165–167°, could be prepared in good yield by the treatment of β-phenyl-β-N-methylpropionic acid with the calculated amount of potassium cyanate in a small quantity of water. Thus, 2.5 g. of the amino acid dissolved in 15 cc. of water was treated with 2 g. of potassium cyanate. The solution was heated on the steam-bath for one and one-half hours, cooled, acidified and filtered immediately. The yield was 2.0 g., m. p. 165–167°. When the hydrochloride of the amino acid was used the product of the reaction was a mixture of the ureido acid, the corresponding hydrouracil, and a little cinnamic acid. The mixture melts from 130–150° with decomposition.

The ureido acid can also be prepared by the partial hydrolysis of the corresponding hydrouracil with dilute alkali.

N-1-methyl-6-phenyl-5,6-dihydrouracil, XVI, m. p. 158–159.5°.—Closure of the ring was brought about quantitatively by heating either the pure ureido acid, XV, or the mixture with 10% hydrochloric acid. The product is soluble in boiling water, from which it crystallizes in long fine needles, and in alcohol, from which it crystallizes in short heavy needles.

Anal. Calcd. for $C_{11}H_{12}O_2N_2$: N, 13.73. Found: N, 13.72, 13.56.

N-1-methyl-6-phenyl-5,6-dihydrouracil can be transformed readily into the corresponding unsaturated compound by treatment with bromine and subsequent expulsion of hydrogen bromide. An ethyl acetate residue can be readily substituted for hydrogen in the N-3-position.

N-1-methyl-6-phenyl-5-bromo-5,6-dihydrouracil, XVII, m. p. 214–215°.—Bromination of N-1-methyl-6-phenyl-5,6-dihydrouracil was brought about in sealed tubes at 100°. When acetic acid was used as solvent, the major product was the 5-bromo compound, but a small quantity of another mono-bromo compound which crystallizes in long needles, m. p. 240–242° without decomposition, was also formed. It was found more convenient to brominate in chloroform solution by the following method. Bromine (4.5 g.) in 40 cc. of alcohol-free chloroform and 5 g. of dihydrouracil were sealed in a Carius tube and heated at 100° for one and one-half hours. After cooling, the solution was diluted to 200 cc. and extracted with a solution of sodium bicarbonate until free from acid. The chloroform was evaporated and the product (6.9 g.) recrystallized several times from boiling alcohol. It precipitates as glistening leaflets which decompose at 214–215°. None of the compound melting at 240–242" was formed.

Anal. Calcd. for $C_{11}H_{11}O_2N_2Br$: N, 9.93. Found: 214–216°, N, 9.92, 10.19; 240–242°, N, 9.95, 10.18.

Boiling the bromine compound for four hours with an equivalent of pyridine in absolute alcohol produced no change. Hydrogen bromide could, however, be driven off by heating, as described below.

N-1-methyl-6-phenyluracil, XVIII, m. p. 194–195°, was prepared by heating the bromine derivative, XVII, at its decomposition point, 215°. Hydrogen bromide is given off, the reaction being complete in fifteen minutes. The yield is quantitative, 3 g. of bromine derivative giving 2.1 g. of uracil. The product was purified by recrystallization from boiling alcohol and from water. No test for bromine could be obtained by fusion with sodium.

Anal. Calcd. for $C_{11}H_{10}O_2N_2$: N, 13.86. Found: N, 13.79, 13.84.

On treatment with sodium and ethyl chloro-acetate the N-3-ethyl acetate derivative, VII, is formed.

Ethyl **N-1-methyl-6-phenyl-5,6-dihydrouracil-N-3-acetate,** XIX, m. p. 70–71°, resulted in good yield from the treatment of N-1-methyl-6-phenyl-5,6-dihydrouracil with sodium and ethyl acetate in the usual manner. The reaction is complete half an hour after the addition of ethyl chloro-acetate. The ester could not be induced to crystallize from the reaction mixture. It was therefore evaporated to dryness and extracted with ether, leaving behind sodium chloride and unchanged N-1-methyl-6-phenyl-5,6-dihydrouracil. The ester was obtained in crystalline form after evaporation of the ether and stirring. From 7.8 g. of N-1-methyl-6-phenyl-5,6-dihydrouracil, 6.6 g. of ester was obtained. The ester is exceedingly soluble in boiling alcohol, but it was purified for analysis by recrystallizations from slightly more dilute solutions in this solvent. Water can be added to precipitate the remainder of the ester.

Anal. Calcd. for $C_{15}H_{18}O_4N_2$: N, 9.66. Found: N, 9.52, 9.42.

Summary

1. The pyrimidine methyl N-1-methyl-6-phenyluracil-N-3-acetate has been synthesized by three series of transformations using 6-phenyluracil, 6-phenyl-5,6-dihydrouracil and benzalmethylamine as starting points.

2. The structure of methyl N-1-methyl-6-phenyluracil-N-3-acetate has been definitely established by its synthesis from benzalmethylamine. The structures of the other uracils and hydrouracils have also been proved by relationships to this ester.

3. β-Phenyl-β-aminopropionic acid has been prepared by the reaction of benzaldehyde, malonic acid and ammonium acetate.

4. The preparation of β-phenyl-β-methylaminopropionic acid from benzalmethylamine is evidence that the formation of β-amino acids from ammonia or amines with aldehydes and malonic acid may take place with the intermediate formation of an imine.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND]

THE DECOMPOSITION OF ETHYL NORMAL-BUTYLACETOACETATE INTO CAPROIC ACID AND METHYL NORMAL-AMYL KETONE

BY NATHAN L. DRAKE AND R. W. RIEMENSCHNEIDER[1]

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A number of methods for the preparation of n-caproic acid have appeared in the literature from time to time.[2] Of the various schemes which have been suggested, the synthetic method described in the article mentioned,[2] starting from ethyl malonate, is the most useful. By use of this method, yields of 74% of the theoretical were obtained.

A synthesis of caproic acid from ethyl n-butylacetoacetate is possible and, inasmuch as ethyl malonate has a molecular weight of 160 compared to 130 for ethyl acetoacetate, the acetoacetic ester method appears at first sight attractive. Prices of raw materials are also much in favor of this method.[3] Consequently, if satisfactory yields can be obtained, the de-

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[1] From a thesis submitted to the Graduate School of the University of Maryland by R. W. Riemenschneider in partial fulfilment of the requirements for the degree of Master of Science.

[2] See Adams and Marvel, THIS JOURNAL, 42, 317–319 (1920), for a brief summary of these methods.

[3] Eastman's "List No. 21" quotes the following: ethyl acetoacetate $7.00 per kg.; ethyl acetoacetate (pract.) $3.00 per kg ; ethyl malonate, $12.00 per kg.; ethyl malonate (techn.) $10.00 per kg.

composition of ethyl n-butylacetoacetate should offer a more economical method of preparing caproic acid than the decomposition of ethyl n-butylmalonate.

Considerable quantities of caproic acid were necessary in a research being conducted in this Laboratory, and it was decided, therefore, to study the reaction mentioned above.

Methyl n-amyl ketone can be prepared in approximately a 60% yield by the decomposition of ethyl *n*-butylacetoacetate[4] under appropriate conditions, and the present paper is a report of a series of experiments on factors affecting the yields of this ketone and caproic acid when ethyl n-butylacetoacetate is decomposed by alkali.

The effect of varying concentrations of alkali on the decomposition of many mono-substituted ethylacetoacetates has been studied, but ethyl n-butylacetoacetate is not among them.

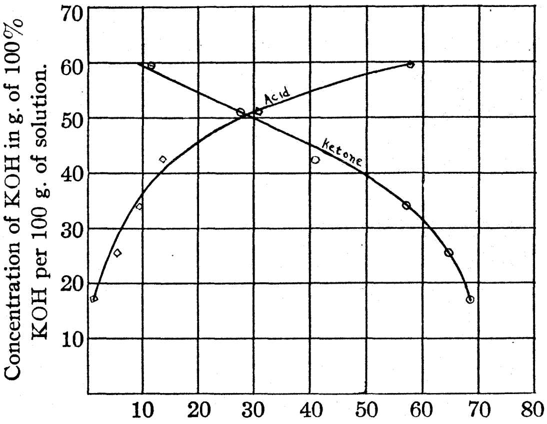

Fig. 1.—The effect of potassium hydroxide concentration on the decomposition of ethyl n-butylacetoacetate (T, 105°).

Experimental

Decomposition of the Ester.—In a round-bottomed three-necked flask fitted with a reflux condenser, a mercury-sealed mechanical stirrer and a separatory funnel, were placed the desired amount of water and potassium hydroxide. The reaction flask was then heated to the desired temperature by means of an oil-bath and the ester[5] added over a period of an hour. The temperature of the oil-bath was read from time to time and the temperatures given in the figures are oil-bath temperatures. Stirring was continued for five hours.

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[4] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 60; see also "Discussion of Results," below.

[5] Prepared according to "Organic Syntheses," John Wiley and Sons, Inc., New York, 1927, Vol. VII, p. 36, b. p. 112–117° at 16 mm. pressure.

Isolation of Methyl *n*-Amyl Ketone.—The alkaline reaction mixture was diluted with 250 cc. of water, except in those cases where dilute alkali was used, and the alcohol and ketone which had been produced were distilled off. Distillation was continued until no more water-insoluble material passed into the distillate. The ketone layer was separated, washed twice with one-half its volume of saturated calcium chloride solution and dried over anhydrous calcium chloride. The water layer of the distillate was again distilled until about half its volume of distillate was collected. From this second distillate the ketone was separated and the distillation process repeated until no appreciable amount of ketone separated from the distillate.

Isolation of n-Caproic Acid.—The alkaline solution from which the ketone had been distilled was acidified with 50% sulfuric acid, with care not to allow the mixture to become unduly hot during acidification. The caproic acid was then extracted with three 100-cc. portions of ether, the combined extracts dried over sodium sulfate and the ether distilled off on a steam-bath. The sodium sulfate used for drying the extracts was washed with a small portion of anhydrous ether which was added to the dried extract. The crude caproic acid remaining was distilled under reduced pressure from a Claisen flask. The fraction boiling from 105 to 110° under 16 mm. was collected. No appreciable quantity of ketone was obtained during this treatment.

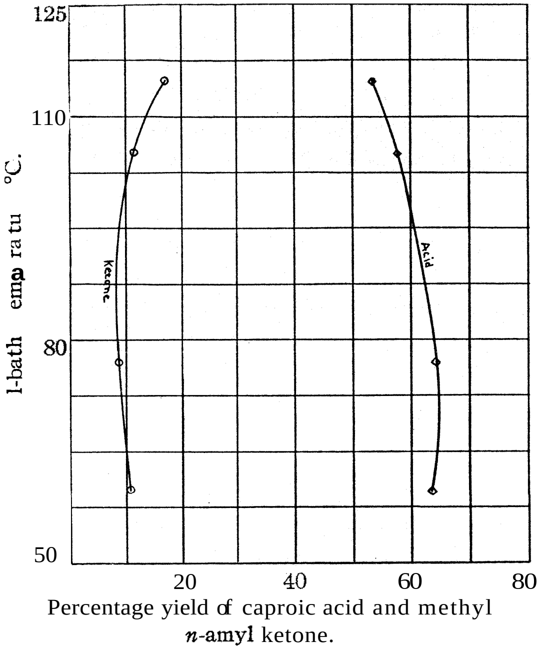

Fig. 2.—The effect of temperature on the decomposition of ethyl n-butylacetoacetate (KOH concentration, 59.5 g. per 100 g. of solution).

Discussion of Results

Figure 1 shows the effect of several concentrations of alkali on the yield of ketone and acid. In the six experiments represented by these curves, the oil-bath temperature was 105° and twelve moles of potassium hydroxide per mole of ester was used. Fifty grams of ester was used in each experiment.

Appreciable formation of acid took place only in the more concentrated solutions. It is interesting to note that increasing the alkali concentration from 51 to 59.5 g. of hydroxide per 100 g. of solution caused an increase in yield of acid from **30.5** to 57.7%.

Best yields of ketone were, of course, obtained in the more dilute solutions. The best yield of ketone obtained here was about 8% higher than that mentioned above.

Figure 2 shows the effect of temperature on the decomposition. It can be seen that the temperature of decomposition is not without effect on the yield, although the effect is not great. The optimum temperature for acid production is about 75°. At this temperature an increase in acid yield from 57.7%, the optimum of Fig. 1, to 64.6% was obtained. The experiments represented by Fig. 2 were carried out using 12 moles of hydroxide per mole of ester and a concentration of 59.5 g. of alkali per 100 g. of solution.

Figure **3** represents a series of experiments carried out to determine the effect of decreasing the number of moles of hydroxide per mole of ester. The temperature of the oil-bath was 75° and the initial concentration of alkali 59.5 g. of hydroxide per 100 g. of solution. Little increase in yield of acid was obtained by using more than eight moles of hydroxide per mole of ester, but a decrease below eight resulted in a very considerable drop in acid yield with a simultaneous rise in the yield of ketone.

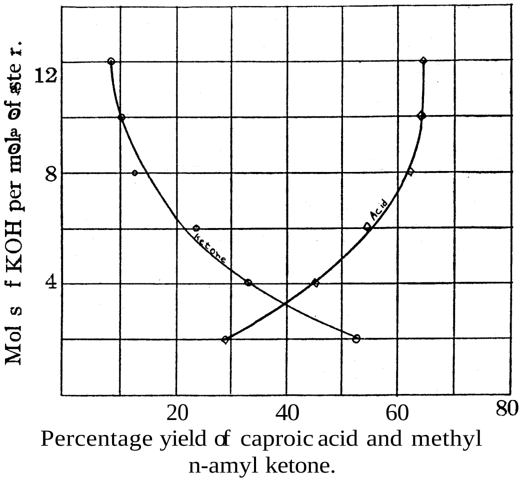

Fig. 3.—The effect of excess alkali on the decomposition of ethyl n-butylacetoacetate (oil-bath temperature, 75°).

In all of the experiments mentioned above the stirring of the reaction mixture was continued for five hours to allow the decomposition of ester to proceed to completion. It is reasonably certain, however, that this period could be considerably shortened. One experiment was conducted in which the time of heating was one hour; the yield of caproic acid was 55.5%. It seemed to us that efficiency of stirring was very important, although no experiments to verify this idea were conducted, and it is believed that with very efficient stirring one hour would have been sufficient to bring the decomposition to completion.

Summary

1. The effects of alkali concentration, excess of alkali and temperature on the decomposition of ethyl n-butylacetoacetate have been studied.

2. Formation of caproic acid in satisfactory yield is possible only in very concentrated alkali.

College Park, Maryland

[CONTRIBUTION FROM THE LABORATORY OF THE TECHNICAL UNIVERSITY OF FINLAND]

SOME NEW MONOSUBSTITUTION DERIVATIVES OF RETENE

BY GUST. KOMPPA AND ERIC WAHLFORSS[1]

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Introduction and Historical

Retene is a hydrocarbon derived from pine tar. This compound, 8-methyl-2-isopropylphenanthrene, m. p. 98–99°, exhibits many peculiarities in its behavior toward ordinary chemical reagents. It is quite stable under certain conditions and will frequently react only if brought into solution and agitated vigorously.

Although a number of investigators have studied the effect of various reagents upon retene, the preparation of only one crystalline mono-substituted product has been reported. This, a monocarboxylic acid, $C_{18}H_{17}$-COOH, m. p. 121–123°, was obtained by Liebermann and Zsuffa[2] by the action of oxalyl chloride, in the presence of aluminum chloride, on a solution of retene in carbon disulfide. Repetition of this experiment from the meager description given resulted, in this research, in the formation of a well-characterized monocarboxylic acid, which after thorough purification and recrystallization melted over 100° higher, 229–231°.

Ekstrand[3] obtained a yellowish oil analyzing for a monochlororetene, $C_{18}H_{17}Cl$, by the action of chlorine gas on crystalline retene. No other monohalogen substitution products of retene have been reported.

The action of nitric acid on retene has been investigated extensively. Concentrated as well as fuming nitric acid readily attacks retene but no crystalline nitro derivatives have thus far been obtained.

The effect of sulfuric acid on retene has been studied by a number of investigators. Knauss[4] observed that sulfur dioxide was evolved when retene was heated with concentrated sulfuric acid above 100". Apparently, however, no sulfonic acid was formed as no soluble barium salt could be isolated. Fritzsche[5] was able to isolate the barium salt of a disulfonic acid, $C_{18}H_{16}(SO_3H)_2$, obtained by the action of a mixture of concentrated and fuming sulfuric acid on retene. Ekstrand[3] was able to identify the free disulfonic acid and its chloride. All his attempts to prepare a monosulfonicacid, despite the use of the most diverse experimental conditions, were fruitless.

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[1] Abstracted from a thesis presented by Eric Wahlforss in January, 1924, to the Faculty of Philosophy of the University of Helsingfors, Finland, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Acknowledgment is made to Dr. L. A. Goldblatt of the University of Pittsburgh in appreciation of the assistance rendered in abstracting this paper from the original Swedish thesis,

[2] Liebermann and Zsuffa, ***Ber.,*** 44, 857 (1911)

[3] Ekstrand, ***Ann.,*** 185, 81 (1877).

[4] Fehling, *ibid.,* 106, 391 (1858).

[5] Fritzsche, *J. prakt. Chem.,* 82, **335** (1861).

Results and Discussion

A well-characterized monocarboxylic acid, $C_{18}H_{17}COOH$, m p. 229–231° was prepared by the method of Liebermann and Zsuffa.[2]

The methyl ester of this acid, $C_{18}H_{17}COOCH_3$, m. p. 96–97°, and the amide, $C_{18}H_{17}CONH_2$, m. p. 224–226°, were prepared. A monocarboxylic acid of retenequinone, $C_{18}H_{15}O_2COOH$, m. p. above 237°, was prepared by the action of chromic acid on the monocarboxylic acid dissolved in glacial acetic acid. This shows that the carboxyl group does not enter the 9- or 10-position in retene.

Attempts to chlorinate retene at 120–130 and 170–180° and to brominate retene dissolved in carbon tetrachloride both in the presence and absence of iodine resulted in the formation of a great variety of products with varying halogen contents but no definite compound could be isolated.

A viscous yellowish oil was obtained when retene dissolved in carbon tetrachloride was chlorinated with chlorine gas. Analysis indicated the formula $C_{18}H_{17}Cl$ for this product. It distilled at a constant temperature of 350–351° at atmospheric pressure but a high percentage of the original oil resinified. The wide range of boiling point, 195–205°, when this product was distilled at 10 mm. pressure would indicate the presence of a mixture. The insolubility of this oil in alcohol together with its analysis and its behavior when subjected to sulfonation indicated that it was at least not a mixture of retene and higher chlorinated derivatives. Oxidation of monochlororetene with chromic acid in acetic acid solution resulted in the formation of retenequinone. This indicates that the chlorine substitutes in the 9- or 10-position in retene.

Boiling the chlorinated product with alcoholic potassium hydroxide and with quinoline did not split off hydrogen chloride. The chlorine atom could not be replaced by iodine by treatment with sodium iodide in acetone or glacial acetic acid solution. No crystalline products were obtained when the monochlororetene was nitrated or sulfonated. Attempts to obtain monohydroxyretene from monochlororetene by Grignard's reaction resulted in the formation of traces of oil which were insoluble in water, aqueous sodium carbonate and mineral acids but soluble in aqueous sodium hydroxide. This oil gave the Liebermann test for phenols.

Methylretene, which could be considered as a link between retene and the resin acids, is of considerable theoretical significance. Attempts to prepare this compound from monochlororetene and methyl iodide with sodium in absolute ether were, however, unsuccessful.

Attempts to prepare a crystalline nitro derivative of retene by the action of nitric acid on retene dissolved in glacial acetic acid; acetyl nitrate in acetic anhydride solution and benzoyl nitrate in carbon tetrachloride solution were all unsuccessful. In one case traces of a yellow nitro derivative, 0.01 g., m. p. 154.5–156.5°, were obtained from 5 g. of retene by the action of acetyl nitrate in carbon tetrachloride solution.

Although retene was sulfonated with chlorosulfonic acid in boiling chloroform solution, no pure crystalline monosulfonic acid was obtained in this research. Two isomeric monosulfonic acids, $C_{18}H_{17}SO_3H$, designated as A-retenesulfonic acid and B-retenesulfonic acid, were obtained by adding concentrated sulfuric acid to vigorously stirred melted retene. Lower temperatures favored the formation of the A-retenesulfonic acid, m. p. 188–189°, and higher temperatures favored the formation of the B-retenesulfonic acid, m. p. 121–123°.

Attempts to isolate and separate the two monosulfonic acids by means of the alkaline earth and lead salts were unsuccessful as, contrary to the general rule for sulfonic acids, these salts are only very slightly soluble in hot water. The sodium, potassium and ammonium salts, however, differ enough in solubility from the other products formed during sulfonation to permit separation. The salts of the B-retenesulfonic acid are much more soluble than the corresponding salts of the A-retenesulfonic acid. The free B-retenesulfonic acid was obtained by the action of sulfuric acid on its barium salt. A-retenesulfonic acid again was isolated directly from the sulfonation mixture.

The formation of quinones, $C_{18}H_{15}O_2SO_3H$, when both the A-retenesulfonic acid and B-retenesulfonic acid were oxidized with chromic acid in acetic acid solution shows that the sulfonic acid group does not enter the 9- or SO-position in retene. Alkaline permanganate is decolorized by the potassium salts of the retenesulfonic acids but no crystalline oxidation products could be isolated.

A number of metallic salts of both retenesulfonic acids were prepared and analyzed. They crystallize with varying amounts of water of crystallization. Fusion of the ammonium sulfonates with alkali leads to the formation of monohydroxy derivatives. The term *retenol* is suggested for monohydroxyretene, $C_{18}H_{17}OH$, in analogy with the corresponding term for monohydroxyphenanthrene.

The methyl ester, $C_{18}H_{17}SO_3CH_3$, m. p. 164–166°, and A-retenol, $C_{18}H_{17}OH$, m. p. 200–202°, were obtained in good yields from the ammonium salt of A-retenesulfonic acid. The picrate of A-retenol melted at 151–152'.

A number of derivatives of B-retenesulfonic acid were prepared. The chloride, $C_{18}H_{17}SO_2Cl$, m. p. 146.5–148°; the amide, $C_{18}H_{17}SO_2NH_2$, m. p. 206–207.5°; the methyl ester, $C_{18}H_{17}SO_3CH_3$, m. p. 117–119° and the potassium salt of the quinone, $C_{18}H_{15}O_2SO_3K$, were obtained in crystalline form. B-retenol, $C_{18}H_{17}OH$, m. p. 158.5–159°, was prepared by fusing the ammonium salt of B-retenesulfonic acid with potassium hydroxide. Its picrate melted at 145–146°, and its acetyl compound, $C_{18}H_{17}OCOCH_3$, at

132–134°. B-retenol when coupled with diazobenzenesulfonic acid developed an orange-red color.

Two attempts to acetylate retene with acetyl chloride in carbon disulfide solution in the presence of aluminum chloride gave no positive results. These, together with other experiments of a negative nature, are omitted from the Experimental Part.

The following derivatives have been prepared in this investigation

Derivatives	Melting point, °C.		
	A =	B =	
$C_{18}H_{17}SO_2OH$	188–189	121–123	
$C_{18}H_{17}SO_2Cl$		146.5–148	
$C_{18}H_{17}SO_2NH_2$		206–207.5	
$C_{18}H_{17}SO_2OCH_3$	164–166	117–119	
$C_{18}H_{17}OH$	200–202	158.5–159	
$C_{18}H_{17}OH$ picrate	151–152	145–146	
$C_{18}H_{17}OCOCH_3$		132–134	
$C_{18}H_{17}COOH$			229–231
$C_{18}H_{17}CONH_2$			224–226
$C_{18}H_{17}COOCH_3$			96–97

Experimental Part

The retene used in these experiments was obtained from that fraction of pine tar boiling above 300°. After purification it possessed a uniform melting point of 98–99°.

Monochlororetene.—A solution of 40 g. of retene in 200 g. of carbon tetrachloride to which a trace of iodine had been added was cooled to 0°. Chlorine gas was then passed through the solution until an increase in weight of 12.2 g. was noted. The solution was allowed to stand overnight at room temperature and was then washed successively with aqueous sodium bisulfite, sodium hydroxide and water. After drying with calcium chloride, the solvent was distilled off and the residue was rectified under reduced pressure. In this way 36.5 g. (79.5% yield) of a yellowish oil boiling at 195–205° (10 mm.) was obtained.

Anal. (Carius) Calcd. for $C_{18}H_{17}Cl$: Cl, 13.20. Found: Cl, 13.13.

This product is nearly insoluble in alcohol but is soluble in ether and petroleum ether. It distilled at 350–351° at atmospheric pressure (747.6 mm.) without appreciable decomposition but left a considerable residue of tar in the distilling flask. A small amount of chlorine-free substance crystallized out on standing. After one recrystallization from alcohol this melted at 94–97°. Mixed with retene, m. p. 98.5°, it melted at 96–97". The distillate was boiled with alcohol to remove any traces of retene. The residue, d_4^{20} 1.1359, was analyzed for chlorine.

Anal. Calcd. for $C_{18}H_{17}Cl$: Cl, 13.20. Found: Cl, 13.30.

The results of refluxing this product for twenty-five hours with 33% alcoholic potassium hydroxide and for half an hour with quinoline indicated that it was not a mixture of retene and retene dichloride.

Oxidation of Monochlororetene.—A solution of 1.1 g. of monochlororetene in 3.5 g. of glacial acetic acid was treated with a solution of 1.9 g. of chromic acid in 10 g. of glacial acetic acid. The mixture was refluxed for half an hour. On cooling 0.4 g. (37.0% yield) of red chlorine-free needles separated out. The melting point, 190–192°, and appearance indicated that this was retenequinone.

Reteoecarboxylic Acid and Derivatives

Retenecarboxylic Acid.—To a solution of 10 g. of retene in 75 cc. of freshly purified carbon disulfide, cooled to $-4°$, were added *23.4* g. of oxalyl chloride and *5* g. of finely pulverized aluminum chloride. After three hours an additional *75* cc. of carbon disulfide and *10* g. of aluminum chloride were added. The mixture was then left at room temperature. When after two weeks no more hydrogen chloride was evolved, the carbon disulfide was filtered off and the residue extracted with ether. The solvent was distilled and the residue boiled with aqneous sodium carbonate. The sodium salt of the carboxylic acid separated out from the solution; yield, *4.4* g. (31.6%). The free carboxylic acid was obtained by boiling the aqueous solution of the sodium salt with very dilute hydrochloric acid. After three crystallizations from benzene the acid melted at *229–231°*. The acid is difficultly soluble in ether, more easily soluble in boiling benzene. It was titrated in alcohol solution with $N/10$ potassium hydroxide: calcd. for *0.1130* g. $C_{18}H_{17}COOH$: *4.06* cc.; found: *3.95* cc.

Sodium Salt.—This salt was prepared by neutralizing an alcohol solution of the free acid with $N/10$ aqueous sodium hydroxide.

The alcohol was distilled off and the salt recrystallized from water. The shining silver scales thus obtained were difficultly soluble in cold water but more easily soluble in hot water. They contain five molecules of water of crystallization. all of which are entirely lost below 136°. After drying the salt was analyzed.

Anal. Calcd. for $C_{18}H_{17}COONa$: Na, *7.66*. Found: Na, *7.50*.

Methyl Ester.—This compound was prepared by refluxing the sodium salt with dimethyl sulfate for five minutes. After recrystallization from alcohol a 51.7% yield of fine, slightly yellow scales, m. p. 96–97°, was obtained.

Anal. Calcd for $C_{20}H_{20}O_2$: C, *82.15;* H, *6.90*. Found: C, *81.70;* H, *6.75*.

Amide.—This compound was prepared from the acid chloride. A mixture of *0.24* g. of retenecarboxylic acid, 1 g. of phosphorus oxychloride and *0.5* ***g.*** of phosphorus pentachloride was heated on a water-bath for ten minutes. The resulting mixture was cooled and poured into ice water. The undissolved part was filtered off, washed, dried in a desiccator and extracted with ether. The ether extract was washed with water, and the ether evaporated, leaving the solid acid chloride; yield, *0.14* g. (54.7%). It was dissolved in benzene and shaken with concentrated ammonium hydroxide. The precipitated amide was filtered off and recrystallized from benzene, m. p. *224–226°*.

Retenequinonecarboxylic Acid.—To a solution of *0 2* g. of the dried sodium salt in *1* g. of glacial acetic acid was added in small portions a solution of *0.38* ***g.*** of chromic acid in *3.5* g. of glacial acetic acid. The mixture was refluxed for twenty minutes. On cooling the retenequinonecarboxylic acid separated out in long needles; yield, *0.13* g. *(63.4%)*. This substance was boiled with hydrochloric acid and recrystallized from glacial acetic acid; m. p. 237–240°. Owing to the dark red color of the acid it was difficult to determine the melting point. When dried for two days over sulfuric acid no loss in weight was observed. The acid was slightly soluble in water and ether, somewhat more soluble in alcohol. It was titrated in very dilute alcohol solution with $N/100$ potassium hydroxide: calcd. for *0.0423* g. of $C_{18}H_{15}O_2COOH$: *13.7* cc.; found: *13.0* cc.

Monosulfonic Acids and Derivatives

A-Retenesulfonic Acid.—To 10 g. of retene heated on an oil-bath to 99° was added *10* g. of sulfuric acid (sp. gr. *1* 84). The acid was at room temperature and was added slowly, with vigorous stirring, to the melted retene. The sulfonation was completed in five minutes, as was indicated by complete solution of a sample in hot water. The sulfonation mixture was poured into *200* g. of hot water. allowed to cool to about 70°

and filtered. After some time a gelatinous mass formed and this was filtered off. The residue was washed first with very dilute sulfuric acid and then with cold water. After drying in a desiccator it was extracted with ether and the residue recrystallized from glacial acetic acid. This gave well-developed scales melting at 188–189°. The acid was titrated in alcohol solution with $N/10$ sodium hydroxide: calcd. for 0.1530 g. of $C_{18}H_{17}SO_3H$: 4.87 cc.; found: 4.75 cc.

Ammonium Salt.—The sulfonation mixture, prepared as above, was poured into 300 g. of hot water, cooled and extracted with ether. The aqueous solution was reheated and concentrated ammonium hydroxide was added. The thick precipitate of ammonium A-retenesulfonate which thus formed was filtered off, washed with water and dried at 135°; yield, 3.85 g. (28.4%).

Methyl Ester.—This compound was prepared by refluxing potassium A-retenesulfonate with dimethyl sulfate. This salt had been obtained by neutralizing an alcohol solution of the free acid with potassium hydroxide. An 88.2% yield was obtained. The thin small scales of the methyl ester after recrystallization from methyl alcohol melted at 164–166°.

Anal. Calcd. for $C_{19}H_{20}SO_3$: C, 69.46; H, 6.14. Found: C, 69.33; H, 6.02.

Potassium A-Retenequinonesulfonate.—To a solution of 0.9 g. of A-retenesulfonic acid in 25 g. of glacial acetic acid was added in small portions a solution of 0.9 g. of chromic acid in glacial acetic acid. The solution was refluxed for half an hour and allowed to cool. As nothing crystallized out, it was evaporated to 10 cc. and again cooled. As precipitation still did not take place the solution was heated and a slight excess of potassium hydroxide was added. On cooling a red substance precipitated. This was washed with cold water and dried in a desiccator; yield, 0.5 g. (45.7%). This product, potassium A-retenequinonesulfonate, was easily soluble in hot water.

Anal. Calcd. for $C_{18}H_{15}O_5SK$: K, 10.23. Found: K, 9.99.

A-Retenol.—To 10 g. of potassium hydroxide and a few drops of water, heated in a nickel crucible to 220°, was added slowly 1 g. of ammonium A-retenesulfonate. The temperature was then increased to 270° and the fused potassium compound of A-retenol floated to the top. Not more than fifteen minutes should elapse from the time of the first addition of the salt. The entire mixture was then poured on to a copper plate, allowed to cool and dissolved in 1000 cc. of hot water.

The solution was filtered through a warm water filter and the phenol was precipitated with dilute sulfuric acid. After carefully decanting the supernatant liquid, the precipitated A-retenol could readily be filtered. It was washed thoroughly with water and with dilute aqueous sodium carbonate, dried in a desiccator and extracted with ether. The ether solution was thoroughly washed with water and aqueous sodium carbonate. The ether extract gave 0.4 g. of solid phenol (53.0% yield). Fine yellowish needles melting at 200–202" were obtained after three crystallizations from xylene. A-retenol is easily soluble in ether, boiling benzene and xylene, soluble in warm alkali and alcohol, but insoluble in aqueous sodium carbonate and sodium bisulfite. The picrate of A-retenol was obtained by mixing equivalent quantities of alcohol solutions of the components. The ruby red needles of this compound melted at 151–152°. A-retenol gave a positive Liebermann test for phenols. Ferric chloride imparted a slightly green color to an alcohol solution of the phenol.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.35; H, 7.25. Found: C, 86.13; H. 7.22.

B-Retenesulfonic Acid.—To 10 g. of retene heated on an oil-bath to 200° was added 10 g. of sulfuric acid (sp. gr. 1.84). The acid was at room temperature and was added slowly with vigorous stirring. The sulfonation was completed in two minutes. The product was poured into 300 g. of hot water. The solution was boiled and an excess of concentrated ammonium hydroxide was added. It was cooled, allowed to stand for twenty-four hours and filtered. The precipitated ammonium salt was washed with cold water and dried; yield, 5.0 g. (35.4%). The salt was redissolved in hot water and boiled with aqueous sodium hydroxide. An excess of barium chloride was added to the solution of the sodium salt, made slightly acid with hydrochloric acid, and the barium salt was filtered off and washed thoroughly. After treatment with the calculated amount of sulfuric acid, the free B-retenesnlfonic acid was obtained in the form of colorless scales. These, when dried for two weeks in a desiccator, melted at 121–123°. The acid was titrated with $N/10$ potassium hydroxide: calcd. for 0.1154 g. of $C_{18}H_{17}SO_3H$: 3.67 cc.; found: 3.65 cc.

Salts.—A number of salts of B-retenesulfonic acid were prepared and analyzed.

Ammonium Salt.—Prepared from the free acid, m. p. 121–123°, and ammonium hydroxide. Solubility: 0.1082 g. of salt in 100 g. water at 17°; more soluble at 100°. The salt, which crystallized without water of crystallization, was dried at 150" and analyzed. Calcd for $C_{18}H_{21}SO_3N$: C, 65.21; H, 6.39; S, 9.68; N, 4.23; found: C, 65.09; H, 6.34; S (Carius), 9.60; N (Kjeldahl), 4.11.

Sodium Salt.—Prepared from the free acid and aqueous sodium hydroxide. Crystallized from water in white scales, which, air dried, contained three molecules of water. Two molecules were lost at 110° and the third at 150". Solubility: 0.0726 g. of the anhydrous salt in 100 g. of water at 17°; more soluble at 100". The salt was dried at 150° and analyzed. Calcd. for $C_{18}H_{17}SO_3Na$: Na, 6.84; found: Na, 6.96.

Potassium Salt.—Prepared from the free acid and aqueous potassium hydroxide. Crystallized from water as crystalline powder without water of crystallization. Solubility: 0.0824 g. of salt in 100 g. of water at 17°; only slightly more soluble at 100°. The salt was dried at 150° and analyzed. Calcd. for $C_{18}H_{17}SO_3K$: K, 11.10; found: K, 11.00.

Barium Salt.—Prepared from the sodium salt and barium chloride. Precipitated as a crystalline powder which, air dried, contained two molecules of water; both were lost when dried over sulfuric acid. Solubility: 0 0848 g. of anhydrous salt in 100 g. of water at 17°; sparingly soluble at 100". The salt was analyzed. Calcd. for $(C_{18}H_{17}SO_3)_2Ba$: Ba, 17.99; found: Ba, 17.70.

Strontium Salt.—Prepared from the sodium salt and strontium chloride. Precipitated as a crystalline powder, which, air dried, contained four molecules of water; all four molecules were lost when dried over sulfuric acid. Solubility: 0.1016 g. of anhydrous salt in 100 g. of water at 17°; sparingly soluble at 100°. The salt was anzlyzed. Calcd. for $(C_{18}H_{17}SO_3)_2Sr$: Sr, 12.27; found: Sr, 12.28.

Calcium Salt.—Prepared from the sodium salt and calcium chloride. Precipitated as a crystalline powder, which, air dried, contained four molecules of water; all four molecules were lost when dried over sulfuric acid. Solubility: 0.1166 *g.* of anhydrous salt in 100 g. of water at 17°; sparingly soluble at 100°. The salt was analyzed. Calcd. for $(C_{18}H_{17}SO_3)_2Ca$: Ca, 6.01; found: Ca, 6.00.

Copper Salt.—Prepared from the free acid and copper carbonate. Crystallized as light green scales, which, air dried, contained five molecules of water: all five molecules were lost below 150°. Solubility: 0.1572 g. of anhydrous salt in 100 g. of water at 17°; more soluble at 100°. The salt was analyzed. Calcd. for $(C_{18}H_{17}SO_3)_2Cu$: Cu, 9.21; found (CuO): Cu, 8.91.

Chloride.—Prepared from potassium B-retenesulfonate in a manner similar to that described for the chloride used in the preparation of retenecarboxylic acid amide; yield, 68.8%. Recrystallization from benzene gave colorless prisms, m. p. 146.5–148°.

Anal. (Carius) Calcd. for $C_{18}H_{17}SO_2Cl$: Cl, 10.66; S, 9.64. Found: Cl, 10.55; S, 9.79.

Amide.—Prepared from the chloride of B-retenesulfonic acid and ammonium hydroxide; yield, 31.9%; colorless scales, m. p. 206–207.5".

Anal. Calcd. for $C_{18}H_{19}SO_2N$: N, 4.47. Found: N, 4.16.

Methyl Ester.—Prepared from ammonium B-retenesulfonate and dimethyl sulfate; yield, 73.8%. Recrystallization from methyl alcohol gave colorless needles, m. p. 117–119°.

Anal. Calcd. for $C_{19}H_{20}SO_3$: C, 69.46; H, 6.14. Found: C, 69.39; H, 6.02,

Potassium **B-Retenequinonesulfonate.**—To a solution of 2 g. of potassium B-retenesulfonate in 10 g. of glacial acetic acid was added, in small portions, a cold solution of 3.8 g. of chromic acid in 35 g. of glacial acetic acid. The solution was refluxed for about half an hour and on cooling 1.2 g. (55.3% yield) of orange colored scales crystallized out. This product, potassium B-retenequinonesulfonate, was easily soluble in hot water.

Anal. Calcd. for $C_{18}H_{15}O_5SK$: K, 10.23. Found: K, 10.01.

B-Retenol.—Prepared from ammonium B-retenesulfonate by the method used for A-retenol. The temperature, however, was not allowed to exceed 240°; yield, 66.37%. Recrystallization from xylene gave slighly yellowish scales, m. p. 158.5–159°. B-retenol is easily soluble in ether, alcohol, benzene and nitrobenzene; soluble in aqueous sodium hydroxide, but insoluble in sodium carbonate and sodium bisulfite. The picrate of B-retenol, small orange-red scales, melted at 145–146°. B-retenol gave a positive Liebermann test for phenols. Ferric chloride imparted a green color to an alcohol solution of the phenol.

Anal. Calcd for $C_{18}H_{18}O$: C, 86.35; H, 7.25. Found: C, 86.14; H, 7.26.

Acetyl-B-retenol.—Prepared from B-retenol, alkali and acetic anhydride. Recrystallization from alcohol gave fern-like crystals, m. p. 132–134°.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.15; H, 6.90. Found: C, 82.09: H. 7.00.

B-Retenol Sodium Azobenzenesulfonate.—B-retenol readily coupled with diazo benzenesulfonic acid, giving a red dye which dyed, wool and silk cherry-red.

Summary

Only two mono-substituted derivatives prepared from retene have been reported previously in the literature: monochlororetene and a monocarboxylic acid, m. p. 121–123°. The preparation of mono-substituted products of retene has been the object of this investigation.

Sulfonation gave two well-defined monosulfonic acids. They were isolated by means of the ammonium or sodium salt. These were used in the preparation of a number of derivatives; the most interesting was the monohydroxy derivative, retenol. Only one retenol coupled with diazo compounds. An attempt to determine the position of the sulfonic acid group by oxidation with chromic acid resulted in the formation of retenequinonesulfonic acid, showing that this group did not enter the 9- or 10-position in retene. Chlorination of retene resulted in an oil, monochlororetene, the individuality of which was not definitely established. Oxidation of this product with chromic acid gave retenequinone. Action of oxalyl chloride on retene resulted in the formation of a monocarboxylic acid, m. p. **229–**

231°. A few derivatives were prepared. Oxidation with chromic acid gave retenequinonecarboxylic acid.

HAMMERMILL PAPER COMPANY
ERIE, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE FORMATION OF A COMPLEX MIXTURE OF MANY RMgX COMPOUNDS FROM THE REACTION BETWEEN A SIMPLE RX COMPOUND AND MAGNESIUM

BY HENRY GILMAN AND NINA B. ST. JOHN

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Introduction

The simplest expressions for the reaction between an RX compound and magnesium in ether are the following

$$RX + Mg \longrightarrow RMgX \qquad (I)$$

$$2RX + Mg \longrightarrow R{\cdot}R + MgX_2 \qquad (II)$$

Reaction II is the chief side reaction in the preparation of Grignard reagents, and the extent of this reaction varies markedly with the nature of the RX compound, the relative proportions of reactants and experimental conditions.[1] The hydrocarbon (or their equivalent) by-products are not pure R·R compounds, but may contain R(+H) and R(–H) compounds[2] as well as R·R compounds having R-groups unlike those contained in the original RX compound.[3]

Furthermore, Reaction I gives an incomplete picture of the more important compounds contained in Grignard solutions inasmuch as these reagents are involved in the following equilibria[4]

$$2RMgX \rightleftarrows R_2Mg + MgX_2 \qquad (III)$$

$$RMgX \rightleftarrows R- + -MgX \qquad (IV)$$

In short, a Grignard reagent is not simply an RMgX compound, but a mixture of RMgX, R_2Mg, MgX_2, R– and –MgX[6] in a series of equilibria

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[1] Gilman, Zoellner and Dickey, THIS JOURNAL, 51, 1576, 1583 (1929); Gilman and McGlumphy, *Bull. soc. chim.*, 43, 1322 (1928); Gilman and Zoellner, THIS JOURNAL, 52, 3984 (1930).

[2] Gilman and Fothergill, *ibid.*, 50, 3334 (1928).

[3] Gilman and Kirby, *ibid.*, 51, 1571 (1929).

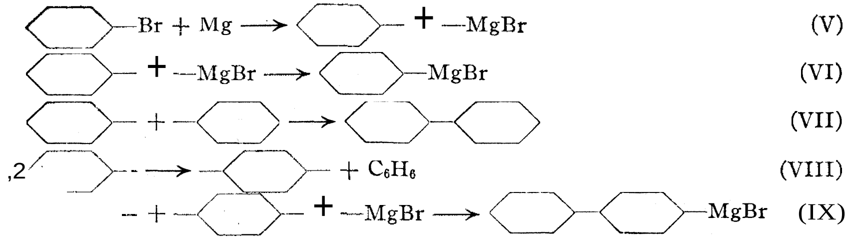
[4] Gilman and Fothergill, *ibid.*, 51, 3149 (1929); Gilman and Zoellner, *ibid.*, 52, 3984 (1930). These articles contain leading references to other work. For recent related studies see Gomberg and Bachmann, *ibid.*, 52, 2455 (1930); Bachmann, *ibid.*, 52, 3287 (1930).

[5] Gilman and Brown, *ibid.*, 52, 1128 (1930). This article contains leading references to the chemistry of the interesting magnesious halides or the binary systems (MgX_2 + Mg) of Gomberg and co-workers. Better reviews of these systems are to be had in the chapters entitled "Metallo-Organic Compounds," in Vol. III (1927–1928) and Vol. IV (1928–1929) of the Annual Survey of American Chemistry, published for the National Research Council by the Chemical Catalog Co. of New York.

with only additional experiments to determine the extent of the equilibrium in Reaction III and the degree of dissociation illustrated by Reaction IV.

When the halide used to prepare the Grignard reagent contains two or more halogens which are reactive toward magnesium, then it is theoretically possible to have an infinite number of Grignard reagents. This[6] development has been illustrated with the relatively simple *p*-dibromobenzene, BrC_6H_4Br. Obviously, with an infinite number of organomagnesium halides derivable from a simple dihalogen compound, there is also present an infinite number of equilibria and dissociation reactions (III and IV).

This very complex state of affairs is apparently not restricted to organomagnesium halides prepared from a polyhalogen compound. It now appears that the reaction of a simple RX compound, having but one halogen, can give rise to a very complex mixture of RMgX compounds. The explanation for such mixtures almost certainly lies with the initial and intermediate formation of free radicals. If we select the reaction between bromobenzene and magnesium as a type, we have the following general representation[7]



That is, the first[8] step in the reaction between an RX compound and magnesium is the formation of free radicals. These radicals may unite (Reaction VI) to give the RMgX compound; or the R-groups may unite to give the coupling (R·R) compound (Reaction VII); or the radical may disproportionate to give new free radicals, like the *p*-phenylene radical in Reaction VIII; and the radicals (mono or polyvalent) may combine with each other and with the –MgX (or its equivalent, MgX_2 + Mg) or with magnesium to give a miscellany of Grignard reagents.

[6] Gilman, Beaber and Jones, *Rec. trav. chim.*, *48*, 597 (1929).

[7] Gomberg and Bachmann, THIS JOURNAL, 49, 236 (1927); Gilman and Zoellner *ibid.*, 52, 3984 (1930); and, particularly, Bachmann and Clarke, *ibid.*, 49, 2089 (1927), for an excellent theoretical and experimental development of the mechanism of the Wurtz-Fittig reaction.

[8] We are omitting here the probable prior formation of oxonium compounds with ether and the several possible coordination formations involving each of the participating elements [Gilman and Fothergill, *ibid*, 51, 3149 (1929)]. See, also, Gilman and Zoellner, *ibid.*, 52, 3984 (1930), and Gilman and Brown, *ibid.*, 52, 5045 (1930), for that interpretation involving combination of free radicals with magnesium.

We have illustrated the formation of but one RMgX compound other than phenylmagnesium bromide: namely, *p*-biphenylmagnesium bromide (Reaction IX). This has been done advisedly because we now have experimental evidence for the formation of *p*-phenylbenzoic acid, *p*-$C_6H_5C_6H_4$-COOH, when carbon dioxide is passed into a Grignard reagent (or reagents) prepared from bromobenzene and magnesium.

There is no reason, a *priori,* for confining consideration to the reactions (V) to (IX) as we have done. For example, it appears altogether probable that two phenyl radicals might disproportionate to give not only *p*-phenylene (Reaction VIII), but also a lesser quantity of *o*-phenylene.[3] Furthermore, multiples of these phenylene radicals might unite with a phenyl radical and $-MgBr$ (Reaction IX) to give $C_6H_5(C_6H_4)_nMgBr$.[9] Many other combinations are possible, such as the union of a phenylene radical with two $-MgBr$ groups to give $BrMgC_6H_4MgBr$.

The theoretical possibilities of even more complex mixtures are patent with the use of halides like the mono-bromotoluenes or benzyl chloride, inasmuch as we have here the opportunity of free radicals formed from the side chain as well as from the nucleus. Finally, we are unaware of any valid objection to a like condition with *alkyl*magnesium halides. A good case has been made for the short life of alkyl radicals,[10] and their disproportionation,[2] as well as for the disproportionation and rearrangements of arylalkyl radicals such as benzyl.[3] If we grant the possibility of an alkyl radical to disproportionate to an alkylene[11] radical by analogy with Reaction VIII, and to rearrange to a different free radical, then there exists the same opportunity for the formation of a complex mixture of Grignard reagents from a simple mono-halogen[12] alkyl halide.

The above development has a theoretical reasonableness and part of it, as mentioned, has found experimental confirmation. Fortunately, the extent of these many possible side reactions leading to the formation of complex mixtures of RMgX compounds is strictly limited because of preferential reactions. If a so-called single Grignard reagent is in reality very slightly contaminated with many other RMgX compounds, then the products obtained from them and reactants are also approximately of a like

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[9] Actually, the residues which yielded *p*-phenylbenzoic acid contained highly complex, intractable materials which so far have resisted purification, primarily because of the small quantities of starting materials used.

[10] Paneth and Hofeditz, *Ber.,* **62B, 1335** (1929).

[11] The general evidence for alkylene (or bivalent) radicals is at present hardly as convincing as that for alkyl (or trivalent) radicals and although there is essentially no experimental evidence for monovalent carbon radicals, one can conceive of an alkylene group acting as a donor of hydrogen in its disproportionation reactions.

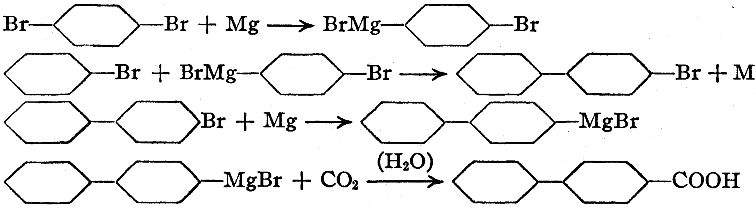
[12] With polyhalogen-alkyl compounds there is, of course, the same opportunity for an infinite number of Grignard reagents that is present in the case of *p*-dibromobenzene (see **Ref. 6** of this paper).

degree of impurity. One important conclusion to be drawn from the several studies is that the world of organic chemicals is relatively "impure." This is hardly a situation peculiar to organomagnesium compounds[2] because it is altogether likely that most reactions of organic chemistry are accompanied by side reactions which give rise to slight impurities. Ordinarily these trivial side reactions deserve no consideration and get no consideration partly because the extent of impurities appears to be of no apparent consequence[13] and partly because we are blissfully ignorant of the impurities for the reason that our present analytical procedures do not reveal them.[14]

Discussion of Results

The isolation of *p*-phenylbenzoic acid came as a result of studies on the purported addition of RMgX compounds to an ethylenic linkage. In order to determine whether phenylmagnesium bromide might add to 1,1-diphenylethylene, $(C_6H_5)_2C{=}CH_2$, in solvents other than ether, the reactants were heated, and then the mixture was carbonated. If no addition took place, then benzoic acid alone should result: However, if some addition occurred a new Grignard reagent would result and this on carbonation would reveal itself by affecting the melting point and neutralization equivalent of the benzoic acid formed from the excess of phenylmagnesium bromide.[15] The acid obtained from this reaction was impure, and in order to identify the acidic impurity the benzoic acid was carefully removed, leaving a small quantity of p-phenylbenzoic acid.

The p-phenylbenzoic acid was also obtained in a like very small quantity when no diphenylethylene was present. There is a possibility that the *p*-phenylbenzoic acid, or the *p*-biphenylmagnesium bromide from which it was formed, came from impurities in the bromobenzene. The following reactions illustrate one of several possible methods for its formation.



(X)

(XI)

(XII)

(XIII)

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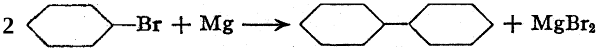
[13] We say "no apparent consequence" advisedly, because there is always the irritable or pleasant phenomenon of catalysis due to small impurities to plague or to delight us depending on one's point of view.

[14] We are confident that other Grignard reagents postulated as being formed in small quantities will be characterized in large-sized runs. In this connection see Footnote 10 of Ref. 3 of this paper on the special contributions to be made to such problems by manufacturers and dealers in research chemicals.

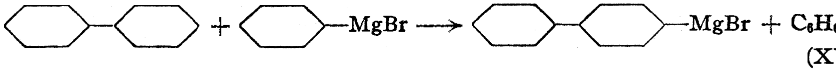
[15] Leading references to the application of this and other devices to establish the non-addition of RMgX compounds to an ethylenic linkage may be traced from an article by Gilman and Schulz, THIS JOURNAL, 52,3588 (1930).

Reaction X is plausible because small quantities of *p*-dibromobenzene might be present in supposedly pure bromobenzene, and if so it would readily react with magnesium to give the mono-Grignard reagent.[6] However, Reactions XI and XII are less reasonable because they take place with uncommon difficulty and to a limited extent.[16] The bromobenzene used by us was highly purified. Not content with this, we prepared some bromobenzene by a reaction other than that used technically (the bromination of benzene): namely, a Sandmeyer reaction starting with freshly distilled and pure aniline. We do not say that no *p*-dibromobenzene is formed in such a reaction, but it does appear to be distinctly superior to the reaction of direct bromination and should yield a bromobenzene as pure and as free of dibromobenzene as that obtained by any reaction. This bromobenzene also yielded p-phenylbenzoic acid.

There is another possible explanation for the *p*-biphenylmagnesium bromide and this is illustrated by the reactions



(XIV)



(XV)

The diphenyl of Reaction XIV is always formed to a small extent[17] in the preparation of phenylmagnesium bromide, and Reaction XV has been postulated in an interpretation of the Wurtz reaction using sodium.[18] However, the metathesis pictured in Reaction (XV) has been shown not to apply with Grignard reagents, even at elevated temperatures.[19] To further test the unlikelihood of this reaction, the phenylmagnesium bromide was prepared and heated in the presence of a large quantity of diphenyl, but there was no increase in the yield of p-phenylbenzoic acid on subsequent carbonation.

No p-phenylbenzoic acid was isolated from a 0.5 mole preparation of phenylmagnesium bromide in ether. Very likely the preparation of this Grignard reagent at more elevated temperatures, with no ether, and with an uncommonly large initial excess of bromobenzene gives a higher concentration of phenyl radicals.

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[16] This applies to reactions in ether and not to those in the absence of ether and in the presence of an excess of hot bromobenzene, the condition of our experiments The difficulty mentioned here is even greater when chlorobenzene is used because of its distinctly lesser activity than bromobenzene to magnesium. Notwithstanding this, we did get a small quantity of p-phenylbenzoic acid from the preparation of phenylmagnesium chloride in the absence of ether.

[17] The extent of this side reaction can be markedly decreased with the use of an excess of magnesium; see Gilman and Fothergill, *Iowa State Coll. J. of Science*, **4**, **351** (1930).

[18] Bachmann and Clarke, This Journal, 49,2089 (1927).

[19] Gilman and Leermakers, *Rec. trav. chim.* **48**, 577 (1929); see also, Gilman and Leermakers, *ibid.*, 49, 208, **532** (1930).

Phenylmagnesium chloride prepared in the absence of ether also gave some p-phenylbenzoic acid.[20]

Experimental Part

In a typical preparation, 470.7 g. (3.0 moles) of bromobenzene was refluxed with 6.1 g. (0.25 atom) of magnesium and a crystal of iodine for one hour in a flask provided with a trap[21] to exclude air. The mixture was cooled and then carbonated. A positive color test[22] for Grignard reagent was obtained even after an eighteen-hour passage of carbon dioxide. The weight of crude benzoic acid was 10.05 g. or 32.93%, and it melted at 104–106". Purification by crystallization from hot water gave benzoic acid melting at 122" and a dark brown oily residue which was essentially insoluble in water. This residue on crystallization from benzene gave 0.15 g. of p-phenylbenzoic acid. The p-phenylbenzoic acid was converted to its methyl ester and the identity of both the acid and the ester was confirmed by respective mixed melting point determinations with authentic specimens. Wherever elsewhere p-phenylbenzoic acid was isolated it was identified by a mixed melting point determination.

In order to test the validity of Reaction XV, 50 g. (0.32 mole) of diphenyl was added to 470.7 g. (3 moles) of bromobenzene and 6.1 g. (0.25 atom) of magnesium. After refluxing the mixture for twelve hours it was cooled to 0° and then carbonated for twelve hours. The viscous violet colored mixture gave a negative test for Grignard reagent.[22] The products recovered were a few crystals (not weighed) of p-phenylbenzoic acid, 4.23 g. of benzoic acid and 43.6 g. or 87.2% of the diphenyl.

Using the same proportions of reactants (but omitting the diphenyl) the yield of p-phenylbenzoic acid was 0.02 g. In this experiment the bromobenzene was that prepared from aniline.[23]

Phenylmagnesium bromide (0.3 mole) was prepared in a sealed tube[24] by heating for one hour at 150°, extracted by ether and then carbonated.[25] The yield of *p*-phenylbenzoic acid was 0.6 g. In this method of preparation the reaction between bromobenzene and magnesium is unusually rapid, and actually appears to proceed of itself on the local application of heat. The preparation in an open flask (in the absence of ether) goes much more slowly and so may give rise to a lower concentration of phenyl radicals.

Phenylmagnesium chloride was prepared20 in a like manner from 21.8 g. (0.25 mole) of chlorobenzeneand 7.3 g. (0.3atom) of chlorobenzene, transferred to a flask containing 337.5 g. (3.0 moles) of chlorobenzene, refluxed for thirty minutes and then cooled and carbonated. The yield of crude benzoic acid melting at 104–105° was 9.26 g. (30.35%), and from this was isolated a very small quantity of p-phenylbenzoic acid. It is interesting to note that phenylmagnesium chloride in chlorobenzene is carbonated more rapidly than is phenylmagnesium bromide in bromobenzene.

Summary

The carbonation of phenylmagnesium bromide and of phenylmagnesium

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[20] It has been suggested that it would be interesting to know how iodobenzene and magnesium behave in this reaction, With sodium and chlorobenzene (see Ref. 18 of this paper), there is formed a relatively large quantity of o-phenylene radicals.

[21] Gilman and Hewlett, *Rec. trav. chim.* 48, 1124 (1929).

[22] Gilman and Schulze, THIS JOURNAL, 47,2002 (1925).

[23] This bromobenzene was synthesized by Catherine Vinton.

[24] See, Gilman and Brown, THIS JOURNAL, 52,3330 (1930), for a description of this method for the preparation of some Grignard reagents.

[25] This experiment was carried out by K. E. Marple.

[26] By R. E. Brown.

chloride, each prepared in the absence of ether, gave in addition to benzoic acid very small quantities of *p*-phenylbenzoic acid, $C_6H_5C_6H_4COOH$. The formation of the latter acid is almost certainly due to free phenyl radicals initially developed in the preparation of the C_6H_5MgX.

Attention is directed to the theoretical, and in some cases practical, formation of a large and complex variety of Grignard reagents starting with a single and simple RX compound. Although the degree of these side reactions is fortunately very limited and in most cases insignificant, it emphasizes the difficulty or impossibility of preparing absolutely pure compounds. This difficulty is undoubtedly not confined to organo-magnesium compounds.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE CHEMISTRY OF THE LIPOIDS OF TUBERCLE BACILLI. XXI. THE POLYSACCHARIDE OCCURRING IN THE PHOSPHATIDE FROM THE HUMAN TUBERCLE BACILLI[1]

BY R. J. ANDERSON AND E. GILMAN ROBERTS[2]

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Introduction

Previous investigations in this Laboratory of the water-soluble constituents which are obtained on hydrolyzing the phosphatide **A-3** from the human tubercle bacillus have shown that mannose,[3] inosite[4] and some other reducing sugar, probably invert sugar,[5] are present in about equal amounts in the aqueous solution. The phosphatide fractions isolated from the avian and bovine tubercle bacilli also yielded mannose and inosite on hydrolysis.[6]

In all of these cases prolonged boiling of the phosphatides with dilute acid was necessary before reducing sugars appeared in the solution. It seemed evident, therefore, that the various sugars which were liberated on complete hydrolysis existed in the original phosphatide molecules in firm chemical combination; possibly sugar complexes or polysaccharides

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[1] The present report is a part of a coöperative investigation on tuberculosis and it has been supported partly by funds provided by the Research Committee of the National Tuberculosis Association. (An abstract of this paper was read before the Division of Medicinal Chemistry, at the meeting of the American Chemical Society, Cincinnati, Ohio, September, 1930.)

[2] Holder of a National Tuberculosis Association Fellowship at Yale University 1929–1930.

[3] Anderson and Renfrew, THIS JOURNAL, 52, 1252 (1930).

[4] Anderson, *ibid.*, 52, 1607 (1930).

[5] Anderson, Roberts, and Renfrew, *Proc. Soc. Exptl. Biol. Med.*, *27,* **387** (1930).

[6] Unpublished data.

might be present with which the fatty acids were combined in the form of esters.

We were naturally interested in discovering some evidence of the existence of complex carbohydrates or polysaccharides in the bacillary phosphatides but for a long time we had to be content with the identification of the simple sugars which appeared as cleavage products after hydrolysis. It was difficult to discover a method by which a partial hydrolysis of the phosphatide could be effected without at the same time disrupting the carbohydrate groups.

In the analysis of the so-called purified tubercle bacilli wax[7] we found when this substance was saponified with dilute alcoholic potassium hydroxide that an alcohol-insoluble carbohydrate complex was obtained, while when the wax was hydrolyzed by boiling with acid–alcohol reducing sugars appeared in addition to fatty acids and so-called unsaponifiable wax. Further studies which have not yet been published on the water-soluble cleavage products obtained from the purified wax and from the bovine phosphatide made it seem probable that the polysaccharides or carbohydrate complexes that were present were very stable since only partial hydrolysis could be effected by means of acid–alcohol treatment.

A study has now been made of the cleavage products which are formed when the phosphatide A-3 derived from the human tubercle bacillus is boiled with dilute alcoholic potassium hydroxide. The results obtained were very interesting and entirely unexpected. The phosphatide is insoluble in alcohol but when it is boiled with dilute alcoholic potassium hydroxide the material gradually disintegrates, giving a soap solution of the fatty acids and leaving an amorphous mass of insoluble matter on the bottom of the flask, The latter is easily soluble in water and consists of two components: (a) the potassium salt of an organic phosphoric acid and (b) a neutral carbohydrate. The two products can be separated by dissolving the mixture in water and adding a solution of neutral lead acetate, when the organic phosphoric acid is precipitated as an insoluble lead salt, leaving the carbohydrate in solution. The carbohydrate is precipitated by alcohol as a gummy mass from the aqueous solution after the lead has been removed. The product can be converted into a snow white amorphous powder by pouring its aqueous solution with stirring into absolute alcohol. The substance does not reduce Fehling's solution but after it has been boiled with dilute acid reducing sugar is liberated and after complete hydrolysis it yields about equal parts of mannose and inosite.

The nature of the new compound has not been established definitely but the results so far obtained indicate clearly that the phosphatide contains a new type of polysaccharide. So far as we are aware this is the

[7] Anderson, *J. Biol. Chem.*, **83**, **505** (1929).

first time that a compound of the nature of a polysaccharide or possibly a glucoside composed of mannose and inosite has been found in nature and we propose to name this substance maninositose.

It is an interesting fact that the action of dilute acid and dilute alcoholic alkali upon the phosphatide produces such different cleavage products. When the phosphatide is boiled with dilute acid the molecule is completely disrupted with the formation of fatty acids and glycerophosphoric acid together with reducing sugar and inosite. By the action of hot dilute alcoholic alkali only the fatty acids are split off; the polysaccharide binding is not disturbed and no reducing sugar is liberated. It seems probable, therefore, that the fatty acids are combined as esters with hydroxyl groups in the polysaccharide and the fact that no free glycerophosphoric acid can be isolated from the saponification mixture makes it probable that this substance is also linked in ester combination with the sugar .molecules.

The organic phosphoric acid referred to above was converted into a barium salt. The barium salt is very soluble in water but it is insoluble in alcohol and up to the present time it has been obtained only as a snow white amorphous powder. The substance does not reduce Fehling's solution but after it has been boiled for some time with dilute acid some reducing sugar is liberated. The composition of the substance does not agree with any ordinary hexosemonophosphate since the relation of carbon to phosphorus is approximately C : P = 9 : 2. It is not impossible that it represents a compound of a hexosephosphate with glycerophosphoric acid.

The discovery of maninositose, a bacterial polysaccharide or glucoside of mannose and inosite will open up a new chapter in the study of the function of inosite in cell metabolism. It should also lead to interesting experiments in the synthesis of similar combinations between hexoses such as glucose or mannose and inosite. Biological values or reactions of maninositose are still unknown but various experiments are planned and will be carried out as soon as possible.

Experimental Part

The general properties of the cleavage products obtained on saponification together with methods of separating the organic phosphoric acid and the neutral polysaccharide were worked out in preliminary experiments. Three separate saponifications were conducted in the course of which the various cleavage products were isolated. In all of these experiments very similar results were obtained both qualitatively and quantitatively. The experimental procedure outlined below can, therefore, be recommended as the shortest and most satisfactory.

Saponification of the Phosphatide.—The phosphatide had been prepared by the H. K. Mulford Company from the human tubercle bacillus, strain H-37, according to our original method.[8] The product was a white amorphous powder and its properties were identical with those that we described for the phosphatide A-3. We desire to express our thanks to the H. K. Mulford Company who generously supplied this expensive material.

The saponification[9] was carried out by refluxing a mixture of 18 g. of the phosphatide and 600 cc. of 1% alcoholic potassium hydroxide on the steam-bath for twenty-four hours. The phosphatide agglutinated to a solid mass on the bottom and sides of the flask and the alcoholic solution became slightly straw colored. After the mixture had cooled the insoluble product was a hard brittle mass which could be easily rubbed to a powder. The supernatant liquid was decanted, the flask was rinsed several times with hot alcohol and the solution was reserved for the isolation of the fatty acids.

Examination of the Alcohol-Insoluble Residue.—The material which was insoluble in alcohol was dissolved in 100 cc. of water and the solution was acidified with acetic acid, when a slight scummy precipitate was obtained which consisted mainly of fatty acids which had been occluded in the amorphous mass. The precipitate was filtered off, washed with ether and the extract was combined with the fatty acids obtained from the alcoholic solution.

The aqueous solution and washings, after they had been concentrated under reduced pressure to a volume of about 30 cc., were mixed with 400 cc. of alcohol, when a sticky mass was precipitated. The mixture was allowed to stand until the supernatant liquid was clear; the solution was decanted, and the precipitate was washed with alcohol and dried. The material was dissolved in 10 cc. of water, precipitated by adding alcohol and the supernatant liquid was decanted. After the precipitate had been washed with alcohol and dried, it was dissolved in 60 cc. of water and a slight excess of neutral lead acetate solution was added. The dense amorphous precipitate was filtered off and washed thoroughly with water. The filtrate and washings were saved for the isolation of maninositose.

Isolation of the Organic Phosphoric Acid.—The lead salt was suspended in water, decomposed with hydrogen sulfide and the lead sulfide was filtered off and washed with water. The filtrate, after it had been concentrated under reduced pressure to a volume of about 50 cc., was neutralized with barium hydroxide. A slight amount of an amorphous precipitate separated which was filtered off and washed with water.

This precipitate, which gave a strong reaction for inorganic phosphoric acid, evidently consisted of barium phosphate and it was discarded. The colorless filtrate was mixed with an equal volume of 95% alcohol, when a white amorphous precipitate seprated. The latter was filtered off, washed with 60% alcohol and with alcohol. After the substance had been dried *in vacuo* it weighed 3.15 g. The barium salt was dissolved in a few cc. of water and the perfectly clear solution, after it had been diluted to 40 cc. with water, was precipitated by adding 40 cc. of alcohol. The snow white product after it had been filtered, washed and dried, weighed 3.1 g.

The substance did not directly reduce Fehling's solution but after it had been boiled with an acid for some time it did reduce Fehling's solution.

For analysis the barium salt was dried at 105° *in vacuo* over dehydrite.

Anal. Subs., 0.2223: $BaSO_4$, 0.1481; $Mg_2P_2O_7$, 0.0715. Subs., 0.1722: H_2O, 0.0479; CO_2, 0.0997. Found: C, 15.79; H, 3.11; P, 8.96; Ba, 39.20.

The analytical values agree approximately with the formula $C_9H_{20}O_{14}P_2Ba_2$, which might represent a mixture of equal parts of a hexosemonophosphate and glycerophos-

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[8] Anderson, *J. Biol. Chem.*, 74,525 (1927).

[9] Throughout the various operations air was displaced by nitrogen or carbon dioxide until the fatty acids had been isolated. Freshly distilled solvents were used and the alcohol had been distilled over potassium hydroxide.

phate. It is evident, however, that the substance does pot contain any ordinary hexosemonophosphate, because it does not reduce Fehling's solution until after it has been boiled for some time with an acid. It appears most reasonable, at present, to assume that the compound contains a complex binding which is broken on boiling with acid, yielding a reducing sugar. Further work on this subject will be necessary before we can determine the definite formula of the acid as well as of its cleavage products.

Isolation of **Maninositose.**—The filtrate from the lead acetate precipitation was freed of lead by means of hydrogen sulfide and the lead sulfide was filtered off and washed with water. The clear colorless filtrate was concentrated to a sirup under reduced pressure and the sirup was washed into a beaker with 30 cc. of water. The solution was acidified with 2 cc. of glacial acetic acid and poured with constant stirring into 400 cc. of absolute alcohol, when an amorphous precipitate was obtained. The product was collected on a Buchner funnel, washed thoroughly with absolute alcohol and finally dried in a vacuum desiccator. The snow white amorphous powder weighed 4.4 g. For further purification the product can be reprecipitated a number of times in the same manner but it is recovered practically quantitatively.

The substance is optically active and on moist litmus paper it shows a neutral reaction. It has no definite melting point. When heated it begins to sinter at 100°; it begins to swell or froth at 150° without showing any noteworthy change on further heating, but above 250" it slowly darkens. When the substance is ignited it swells up and burns, leaving a very light voluminous white ash which on further heating forms a fused mass. The ash consists principally of potassium phosphate.

Rotation. 0.5998 g. of substance dried at 60° *in vacuo* over dehydrite was dissolved in water at 23° and made up to 10 cc. In a 1-dm. tube a $= +3.42°$; hence $[\alpha]^{23}_{D}$ $+57°$.

For analysis the substance was dried at 105" *in vacuo* over dehydrite. The loss in weight was 3.5%.

Anal. Found: ash, 16.27; P, 2.33; K, 3.92.

The phosphorus is present in organic combination but it is impossible to state definitely, at present, whether the phosphorus content is due to incomplete removal of the organic phosphoric acid compound or forms an integral part of the carbohydrate molecule.

Hydrolysis of **Maninositose.**—A sample of the neutral carbohydrate which had been repeatedly precipitated from dilute acetic acid with absolute alcohol was hydrolyzed. The snow white amorphous powder, which weighed 1.1 g., was refluxed with 100 cc. of 5% sulfuric acid for four hours. The faintly straw-colored solution was freed of sulfuric acid quantitatively with barium hydroxide and the barium sulfate was removed. The filtrate was concentrated under reduced pressure to 50 cc. and the solution, which showed a slight acid reaction, was neutralized with barium hydroxide. The addition of two volumes of alcohol caused a small amount of an amorphous precipitate to separate. The latter was filtered off, washed with alcohol and dried. The white powder weighed only 0.15 g. and contained organic phosphorus. The properties of the substance resembled those of barium glycerophosphate but the small quantity of the material prevented its definite identification.

Isolation of **Mannose Phenylhydrazone.**—The filtrate from the above-mentioned barium salt was freed of barium quantitatively with sulfuric acid and, after removing the barium sulfate, the filtrate was concentrated to 30 cc. On adding 1 g. of phenylhydrazine dissolved in 2 cc. of alcohol a crystalline precipitate began to separate immediately. After the mixture had stood overnight the crystals were filtered off, washed with water, alcohol and ether. The dried crystals were slightly straw-colored and they weighed 0.55 g. The substance was recrystallized from 50 cc. of hot 60% alcohol and as the solution cooled there separated slowly large colorless rhombic plates which were filtered off, washed and dried. The crystals weighed 0.35 g. and the optical properties were identical with those of mannose phenylhydrazone. The substance melted with decomposition when rapidly heated at 195–196° and there was no depression of the melting point when some of the substance was mixed with a sample of pure mannose phenylhydrazone. The crystal form and melting point definitely identify the substance as mannose phenylhydrazone.

Isolation of Inosite.—The filtrate from the crude mannose phenylhydrazone was shaken with an excess of benzaldehyde for several hours and the precipitated hydrazone was removed by filtration. The solution, after it had been extracted several times with ether, was concentrated under reduced pressure to a sirup and the latter was dried in a vacuum desiccator. A snow-white crystalline residue, free from any sirupy admixture, was obtained that weighed 0.25 g. It was dissolved in a little dilute acetic acid and brought to crystallization by the addition of alcohol. Colorless prismatic needles were obtained that weighed 0.2 g. The crystals gave the Scherer reaction and melted at 225°. There was no depression of the melting point when the substance was mixed with pure inactive inosite prepared from phytin.

It is evident from the results of this analysis that the only products obtained on hydrolyzing the neutral carbohydrate were: (a) a small quantity of a barium salt of an organic phosphoric acid which resembled barium glycerophosphate, (b) mannose, isolated as mannose phenylhydrazone, and (c) inactive inosite. We are forced to the conclusion, therefore, that the carbohydrate consists of a combination of mannose and inosite in the form of a polysaccharide or a glucoside. For want of a better name we designate the substance by the name maninositose.

Isolation of the Fatty Acids.—The alcoholic soap solution, obtained on saponifying the phosphatide, was concentrated to a volume of about 200 cc., diluted with water, acidified with hydrochloric acid, and the fatty acids were extracted with ether. The aqueous solution was saved and examined for glycerol. The ether extract was washed with water until the washings were neutral to litmus and the ether was distilled off. The residue, consisting of the mixed fatty acids, weighed 10.8 g. after it had been dried *in vacuo.* The fatty acids were not separated at this time but they were preserved for future use.

Examination of the Aqueous Solution for Glycerol and Glycerophosphoric Acid.—The acid aqueous solution, which remained after the fatty acids had been extracted, was concentrated to dryness under reduced pressure and the residue was extracted with absolute alcohol. The insoluble potassium salts were removed by filtration, the alcohol was evaporated and the residue was again extracted with absolute alcohol, filtered and diluted with an equal volume of water. The mixture was made faintly alkaline with barium hydroxide when a very slight amorphous precipitate was obtained. The precipitate was filtered off, washed with alcohol and dried. The amount of the substance was very small and since it gave a reaction for inorganic phosphoric acid it evidently consisted of barium phosphate.

The filtrate from the barium precipitate was concentrated to dryness in *vacuo.* The residue was extracted with absolute alcohol, the extract was filtered and the alcohol was distilled off when a slight sirupy residue was obtained. The sirup gave no reduction on boiling with Fehling's solution but when it was heated with acid potassium sulfate a strong odor of acrolein was noted, thus indicating the presence of glycerol.

The alcohol-insoluble potassium salts, which were mentioned above, were dissolved in water and the solution was made faintly alkaline with barium hydroxide. A slight amount of an amorphous precipitate was obtained but there was no further precipitate on adding alcohol. The precipitate gave a reaction for inorganic phosphate and it evidently consisted of barium phosphate. The results of the examination indicate that the aqueous solution contained some free glycerol and some free phosphoric acid but no glycerophosphoric acid could be isolated.

Summary

1. A study has been made of the action of hot dilute alcoholic potassium hydroxide on the phosphatide A-3 from the human tubercle bacillus. When treated in this manner the phosphatide is saponified, yielding an alcoholic soap solution of the fatty acids together with small amounts of free glycerol and phosphoric acid, while an alcohol-insoluble residue remains which consists of a mixture containing a complex organic phosphoric acid and a neutral carbohydrate.

2. The organic phosphoric acid has not been studied fully but when it is boiled with dilute acid it is hydrolyzed with the formation of a reducing sugar which has not yet been identified.

3. The neutral carbohydrate, called maninositose, represents a new type of polysaccharide or a glucoside which on hydrolysis with dilute acid yields mannose and inosite.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE SYNTHESIS OF INDOLYL-BUTYRIC ACID AND SOME OF ITS DERIVATIVES

BY RICHARD W. JACKSON AND RICHARD H. MANSKE

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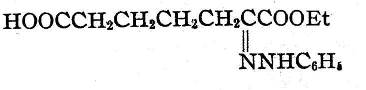
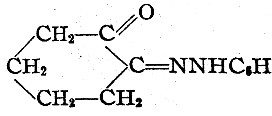
The interest which has of late centered in the metabolism of certain indole derivatives[1,2,3] has made it desirable to prepare new members, particularly some of the higher homologs, of an already known series. For example, to make available a sequence of 3-indolyl acids among which indolyl-propionic acid has heretofore been the highest known homolog, it became desirable to construct the corresponding butyric, valeric and caproic acids. At the same time, the chemical aspects of the syntheses presented several interesting features.

The recently much exploited[4] Japp and Klingemann reaction, when applied to ethyl cyclohexane-1-one-2-carboxylate, produces an excellent yield of the half ester of the phenylhydrazone of α-ketopimelic acid (I)



$$HOOCCH_2CH_2CH_2CH_2\underset{\underset{NNHC_6H_5}{\|}}{C}COOEt$$

I



II

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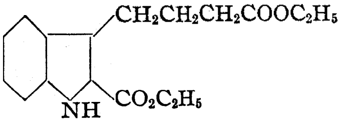
[1] Jackson, *J. Biol. Chem.*, 73, 523 (1927); 84, 1 (1929).

[2] Berg, Rose and Marvel, *ibid.*, 85, 207, 219 (1929).

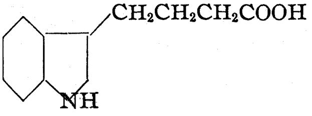
[3] Jackson, *ibid.*. 87, XIV (1930).

[4] Manske, Perkin and Robinson, J. *Chem Soc.*, 1 (1927); Manske and Robinson, *ibid.*, 240 (1927); and others

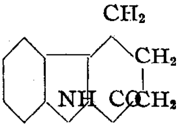
The alternative product, cyclohexane-1,2-dione monophenylhydrazone (11), is formed in only small amounts if at all. Esterification and indole ring closure of the ester (I) take place readily when it is heated in alcohol with sulfuric acid. The dibasic ester (III) thus obtained yields, on hydrolysis and decarboxylation, y-3-indolyl-butyric acid (IV)



III



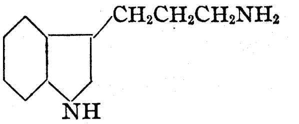
IV



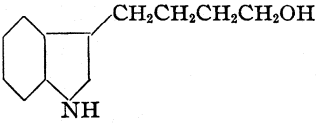
V

2-Ketotetrahydrocarbazole (V) is obtained in small amount during the decarboxylation of the dibasic acid. The temperature required for decarboxylation is presumably sufficient to induce the elimination of water—which is obviously possible and undoubtedly dependent upon the reactivity of the 2-hydrogen atom.

We have converted the indolyl-butyric acid into y-3-indolyl-propylamine (VI) via the methyl ester, the hydrazide, the azide, the urea or the urethan and the phthalimide, and thus there is established a connection between this chain of synthetic products and a substance already known (VI)[5]



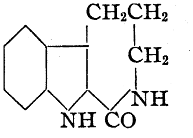
VI



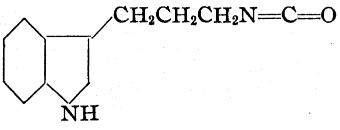
VII

Again, reduction of the ester with sodium and alcohol was found to yield δ-3-indolyl-butyl alcohol (VII); and to make the series more complete, we have, *inter alia*, prepared γ-3-indolyl-propyl alcohol by the reduction of methyl β-3-indolyl-propionate. The preparation of a lower homolog, β-3-indolyl-ethyl alcohol (the tryptophol of Ehrlich) has recently been placed on record by one of us.[6]

Lastly we attempted to synthesize the homo-3-carboline (VIII) by ring closure of the intermediary isocyanate (IX) obtained by heating the azide in an inert medium



VIII



IX

Although the similar synthesis of 2-keto-tetrahydro-3-carboline proceeds with unusual ease from the lower homologous azide,[7] our experiments in

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[5] Majima and Hoshino, *Ber.*, 58, 2042 (1925).

[6] Jackson, *J. Biol. Chem.*, **88**, 659 (1930).

[7] Manske and Robinson, *J. Chem. Soc.*, 240 (1927).

the present case have resulted in only a small amount of the product, which appears, nevertheless, to be the desired substance. Apparently the seven-membered ring is considerably more difficult to form.

Experimental Part

Ethyl **γ-(2-Carbethoxy-3-indolyl)butyrate.**—It was found essential to avoid delay during this preparation as far as the isolation of the phenylhydrazone. To a mixture of 76.8 g. of aniline and 200 cc. of hydrochloric acid (sp. gr. 1.2), 56 g. of solid sodium nitrite was gradually added with constant stirring. Crushed ice was kept floating in the reaction flask during the diazotization. Meanwhile an ice-cold solution of 200 g. of potassium hydroxide in 500 cc. of water was prepared; 136 g. of ethyl cyclohexanone-carboxylate was now poured over 400–500 g. of ice; to this mixture of the ester and ice were added alternately (about ten portions of each) the solutions of the potassium hydroxide and benzenediazonium chloride such that the alkali was always present in excess. Efficient stirring was provided to prevent the formation of any localized acid regions of appreciable extent, and sufficient ice was added from time to time to keep the solution quite cold. None, or at the most only a trace, of the solid potassium salt of the cyclic ester remained at the end of the condensation. The reaction mixture was next acidified with 160 cc. of hydrochloric acid (sp. gr. 1.2) previously diluted and chilled. After standing for a short while, the half ethyl ester phenylhydrazone of a-ketopimelic acid crystallized and could then be filtered and thoroughly washed by suction. It was dried first in the air and then in a vacuum desiccator. A small quantity was recrystallized with some difficulty several times from benzene; it then consisted of an orange colored powder melting at 142–143°.[8] The yield of dried product was uniformly 200 to 204 g. The Fischer indole ring closure and attendant esterification of the free carboxyl group were conveniently effected by refluxing for two and one-half hours with 500 cc. of absolute alcohol and 55 cc. of sulfuric acid (sp. gr. 1.84). The excess alcohol was next largely distilled off under reduced pressure. The oily residue was dissolved in ether–benzene, washed with water and with aqueous sodium bicarbonate and dried over calcium chloride; after the removal of the solvent, the residue was distilled *in vacuo.* The main fraction, obtained at 235° and 7 mm., crystallized on cooling. In order to remove a small amount of oil, the distillates from three runs were united, warmed with 100 cc. of benzene to dissolve nearly all of the ester, cooled and cautiously treated with 400 cc. of petroleum ether. When crystallization was complete, the solid was filtered off and washed with petroleum ether. The yield of colorless product melting at 75–76" was 278 g. (38% of the theoretical calculated on the amount of cyclic ester employed). Recrystallization from benzene–petroleum ether yielded the ester in long needles, melting sharply at 76°.

Anal. Calcd. for $C_{17}H_{21}O_4N$: C, 67.33; H, 6.93; N, 4.62. Found: C, 67.54; H, 7.09; N, 4.75.

The methyl **ester,** although never obtained in as good yield, was prepared from methyl cyclohexanone-carboxylate in a strictly analogous way. The recrystallized ester consisted of colorless fine elongated plates melting at 64°.

Anal. Calcd. for $C_{15}H_{17}O_4N$: N, 5.09. Found: N, 4.74.

During the early part of the distillation of the ethyl and methyl esters described above a colorless crystalline substance sublimed into the condenser and the top of the distillation flask. The identity of the products secured from the two distillations was suspected from their appearance and proved by a mixed melting point determination.

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[8] All recorded melting points are corrected.

Furthermore, the same substance was obtained during the preparation of the lower homologous ester from ethyl cyclopentanone-carboxylate, and a compound of analogous nature was obtained during the course of some unpublished work on the preparation of several methoxy-indole compounds.

Analytical figures and subsequent mixed melting point determination proved the substance in question to be *sym.*-diphenyl-urea (m. p. 240°).

Anal. Calcd. for $C_{13}H_{12}ON_2$: C, 73.58; H, 5.66; N, 13.21. Found: C, 73.82; H, 5.86; N, 13.18.

At present we are not prepared to submit a rational mechanism to account for the universal production of ureas under the conditions of our experiments.

γ-(2-Carboxy-3-indolyl)-butyric Acid.—The hydrolysis of the methyl and ethyl esters of this acid proceeded readily in dilute alcoholic alkali. Subsequent acidification gave quantitative yields of the acid. It was obtained from approximately 50% acetic acid in minute stout prisms melting at 193–194° with loss of carbon dioxide.

Anal. Calcd. for $C_{13}H_{13}O_4N$: N, 5.67. Found: N, 5.56.

Methyl γ-3-Indolyl-butyrate.—The dibasic acid (106 g.) was decarboxylated by heating in an oil-bath at 220° until the evolution of carbon dioxide slowed down somewhat; the decomposition of the melt was completed by elevating the temperature of the bath to 230° for fifteen minutes. The product was esterified by heating under reflux for two hours with 200 cc. of absolute methyl alcohol and 4 cc. of sulfuric acid. The ester isolated in the usual way distilled at 230° at 6 mm.; the yield was 83 g. A small amount of unchanged acid was recovered from the alkaline wash water. The ester solidified completely on cooling and when recrystallized from benzene–petroleum ether was obtained in colorless glistening plates which melted at 73–74°.

Anal. Calcd. for $C_{13}H_{15}O_2N$: C, 71.89; H, 6.91. Found: C, 72.28; H, 7.01.

γ-3-Indolyl-butyric Acid.—The crude decarboxylation residue obtained as described above is difficult to purify directly. It was found more convenient to prepare the monobasic acid by hydrolyzing the distilled methyl ester with alcoholic potash. The acid regenerated from the alkaline solution by acidification was first recrystallized from a large volume of water or from dilute alcohol but the product then tenaciously retained small quantities of water which depressed the melting point several degrees. Recrystallization from a mixture of benzene and petroleum ether gave colorless plates melting sharply at 124°.

Anal. Calcd. for $C_{12}H_{13}O_2N$: N, 6.90. Found: N, 6.77.

The hydrolysis of the monomethyl ester yielded in addition to the acid a small amount of unsaponifiable product which proved to be 2-keto-2,3,4,5-tetrahydrocarbazole the properties of which were first placed on record by Coffey.[9] Recrystallized from alcohol, it melted at 166°. The azine melted at 248°. These melting points agree with those reported by Coffey.

γ-3-Indolyl-butyric Hydrazide.—A mixture of 40 g. of 50% hydrazine hydrate, 54 g. of methyl indolyl-butyrate and 60 cc. of alcohol was placed in a flask equipped with an air-cooled reflux condenser and gradually heated in an oil-bath until the temperature rose to 130°. At the end of an hour, the condenser was removed and the temperature of the bath raised to 140–150° to effect the removal of water, alcohol and excess hydrazine. The product, which crystallized upon standing, was filtered off and washed with cold alcohol. In addition to the first yield of 35 g., a small amount was recovered by evaporating the filtrate. After one recrystallization from alcohol, the hydrazide melted sharply at 112°.

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[9] Coffey, *Rec. trav. chim.*, **42**, 531 (1923).

Anal. Calcd. for $C_{12}H_{16}ON_3$: N, 19.36. Found: N, 19.27.

Di-(γ-3-indolyl-propyl)-urea.—A cooled solution of 10 g. of the above hydrazide in 50 cc. of acetic acid was treated in rapid succession with 200 g. of ice and 4 g. of sodium nitrite dissolved in a small volume of water. The precipitated and washed azide was added in small portions to boiling water and the mixture finally heated until no more decomposition was apparent. The oily urea was washed by decantation and then freed of remaining acid and easily saponifiable matter by heating for a short time with alcoholic potash. The product precipitated by the addition of water was washed with water, dried and then heated under reflux with norite in a large volume of ethyl acetate. The clear filtered solution on evaporation yielded a pale oily residue which crystallized on cautious treatment with ether. The crystals were filtered off, washed with a mixture of ethyl acetate and ether and recrystallized from the same solvents. The yield was 2.3 g. As thus obtained the urea consists of pale yellow plates melting at 124°.

Anal. Calcd. for $C_{23}H_{26}ON_4$: N, 14.97. Found: N, 14.73.

Methyl y-3-Indolyl-propyl-carbamate.—The azide prepared as described above was dissolved in benzene. The solution was clarified with sodium sulfate and then evaporated under reduced pressure at room temperature with frequent addition of dry benzene until all moisture had been removed. The pale yellow residue was treated with 75 cc. of absolute methyl alcohol. The solution was gently warmed until the first vigorous evolution of nitrogen subsided and then heated under reflux for twelve hours with a generous amount of norite. The clear filtrate was then repeatedly evaporated with dry benzene to remove the excess methyl alcohol. The resulting oily residue was taken up in 250 cc. of dry ether. A small amount of insoluble material was filtered off and the filtrate evaporated. Treatment with alcoholic potash removed only inappreciable impurities. Since the urethan could not be induced to crystallize, it was finally distilled in *vacuo* to give 8 g. of an almost colorless and very viscous sirup. This set to a glass on cooling and failed to crystallize in contact with various solvents. Its conversion to the phthalimide is proof of its structure.

γ-3-Indolyl-propyl-phthalimide.—For this preparation, both the urea and the urethan were found to suffice. A mixture of either substance with an equal weight of phthalic anhydride was heated in an oil-bath, finally at 230°, until effervescence ceased. The partially cooled mixture was dissolved in alcohol. The phthalimide was precipitated, while acid products were held in solution, by cautious treatment with sodium carbonate solution. The crystallized product was filtered off, thoroughly washed and recrystallized from hot alcohol, in which it is sparingly soluble. The yield of pure product consisting of pale yellowish plates and melting at 132° was nearly the theoretical amount. It is almost insoluble in ether.

Anal. Calcd. for $C_{19}H_{16}O_2N_2$: N, 9.21. Found: N, 9.03.

The mother liquors from the preparation of the urea were also suitable for making the phthalimide, which in this case was quite pure after two recrystallizations.

γ-3-Indolyl-propyl-amine.—Hydrolysis of the phthalimido compound to the amine was readily accomplished by heating with a slight excess of hydrazine in dilute alcohol. When solution was completed, the alcohol was evaporated and the aqueous solution clarified by filtration through a layer of norite. The phthalyl hydrazide obtained on acidification was filtered off. The amine was then extracted from the basified filtrate. The ethereal extract was dried over potassium hydroxide and concentrated. The residue dissolved in a small volume of acetone was carefully neutralized with dry hydrogen chloride in ether. The crystalline hydrochloride was filtered off and washed with acetone and with ether. A very good yield was secured. In agreement with data reported by Majima and Hoshino,[5] the hydrochloride melted sharply at 170°.

Anal. Calcd. for $C_{11}H_{14}N_2 \cdot HCl$: N, 13.30. Found: N, 13.06.

γ-3-Indolyl-propyl Alcohol.—To 10.2 g. of methyl β-3-indolyl-propionate dissolved in 250 cc. of absolute alcohol[10] was added 17 g. of sodium. The reaction finally was completed by heating for a short time on a steam cone. Water was added and the alcohol distilled off. The alkaline solution was extracted with ether. The residue secured by the evaporation of the ether was distilled *in vacuo* to give 6 g. of a colorless viscous oil. Further purification was effected by conversion to the picrate which on two recrystallizations from benzene was obtained in brick-red stout needles melting at 101°. The alcohol regenerated from the picrate by decomposition with alkali and distilled a second time *in vacuo* was an almost colorless oil which crystallized completely at 0° but which became liquid again at room temperature.

Anal. Calcd. for $C_{11}H_{13}ON$: N, 7.99. Found: N, 7.83.

The alcohol was further characterized by conversion to the phenylurethan formed when the alcohol was heated with a slight excess of phenyl isocyanate. The reaction mixture crystallized readily after it was washed several times with petroleum ether. The derivative was crystallized from hot benzene, in which it is only moderately soluble when cold, to give colorless plates melting at 94°.

Anal. Calcd. for $C_{18}H_{18}O_2N_2$: N, 9.52. Found: N, 9.38.

δ-3-Indolyl-butyl Alcohol.—The reduction of methyl y-3-indolyl-butyrate (85 g.) with sodium (92 g.) and absolute alcohol (1100 cc.) in the manner described above for the lower homolog yielded 57 g. of practically colorless distillate which, on cooling and seeding with a crystal previously prepared from a specimen regenerated from the purified picrate, set to a solid mass of crystals. The material developed a slight reddish color after standing for some time.

The picrate crystallized first from dilute alcohol and then twice from benzene was obtained in ruby-colored needles melting at 102°. The alcohol liberated from the picrate by treatment with alkali was obtained as a colorless oil which slowly crystallized. A small portion plated out on porous tile melted at 32–33°.

Anal. Calcd. for $C_{12}H_{15}ON$: N, 7.40. Found: N, 7.34.

The phenylurethan recrystallized from benzene–petroleum ether melted at 88°. It is readily soluble in the ordinary organic solvents except petroleum ether.

Anal. Calcd. for $C_{19}H_{20}O_2N_2$: N, 9.11. Found: N, 9.14.

There was recovered 13 g. of indolyl-butyric acid on acidifying the alkaline solution remaining from the preparation of the corresponding alcohol. The yield of alcohol based on the ester actually used up was, therefore, 89%.

2-Keto-2,3,4,5-tetrahydro-homo-3-carboline (VIII).—The dried benzene solution of the azide prepared as described under preparation of the methylurethan (p. 5033) was gently heated on the steam-bath until evolution of nitrogen was complete. A stream of dry hydrogen chloride was passed into the solution and heating continued. A considerable amount of resin was precipitated. The clear benzene solution was evaporated to a thin sirup and the crystalline product which separated in the course of several days filtered off and washed with cold alcohol. It was recrystallized first from hot alcohol and then from acetone and was obtained in fine microcrystalline needles melting at 220". The yield was only about 5% of the theoretical. It does not give a color with Ehrlich's reagent immediately but on prolonged boiling a cherry-red color is slowly developed. This behavior is interpreted to signify the opening of the lactam ring with subsequent decarboxylation, the latter process being analogously observed with the similar treatment of other 3-alkylated indole-2-carboxylic acids.

Anal. Calcd. for $C_{12}H_{12}ON_2$: C, 71.96; H, 6.05; N, 13.99. Found: C, 72.12; H, 6.26; N, 13.97.

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[10] Smith, *J. Chem. Soc.*, 1288 (1927).

Experiments are in progress for converting the indolyl-butyl alcohol into the *p*-toluenesulfonyl derivative with the object in view of condensing the latter with ethyl sodio-malonate[11] to obtain indolyl-caproic acid on hydrolysis and decarboxylation. We have succeeded, thus far, in securing a small amount of δ-3-indolyl-butyl malonic acid. It consists of colorless crystals melting at 177°.

Anal. Calcd. for $C_{15}H_{17}O_4N$: C, 65.43; H, 6.23; N, 5.09. Found: C, 65.47; H, 6.23; N, 5.10.

The main product by far from these reactions, however, was found to be present in a neutral fraction secured by ether extraction of an alkaline hydrolysate. The residue from this ether when distilled *in vacuo,* plated out on a porous tile and finally recrystallized from 70% alcohol yielded glistening, colorless plates which alone, or admixed with an authentic specimen of tetrahydrocarbazole prepared for comparison, melted at 117°. Further comparison of the neutral material by means of Ehrlich's color reaction failed, likewise, to disclose any difference.

Whether the ring closure is effected by the action of the acyl chloride directly on the alcohol or whether the toluene-sulfonyl ester eliminates toluene-sulfonic acid in the presence of the hot alcoholic sodium ethylate, we are not prepared to say at present. The latter course would appear to be the more likely one. In any case, however, the mechanism appears to he much the same. We are not familiar with strictly analogous examples of ring closure; the paucity of reactions of this kind is due not only to the lack of suitable orientation but also, we believe, to the absence of sufficient reactivity on the part of the hydrogen atom which must be eliminated along with the hydroxyl group as water.

Summary

1. The synthesis of indolyl-butyric acid has been effected through a procedure involving the application of the Fischer indole ring closure to the phenylhydrazone secured by subjecting ethyl cyclohexanone-carboxylate to the Japp and Klingemann reaction.

2. Along with various other derivatives, indolyl-propyl and -butyl alcohols and 2-keto-2,3,4,5-tetrahydro-homo-3-carboline were prepared. Indolyl-propylamine was synthesized via a new group of indole compounds.

3. The reactivity of the 2-hydrogen atom in the indole ring has been emphasized in light of the formation of 2-ketotetrahydrocarbazole and tetrahydrocarbazole as by-products of certain reactions employed.

4. Indolyl-butylmalonic acid has been synthesized.

NEW HAVEN, CONNECTICUT

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[11] Peacock and Tha, J. *Chem. Soc.,* **2303** (1925).

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

THE REPLACEMENT OF HALOGEN BY HYDROGEN IN ALPHA HALO-KETONES UNDER THE INFLUENCE OF THE GRIGNARD REAGENT

BY C. HAROLD FISHER, THOMAS S. OAKWOOD AND REYNOLD C. FUSON

RECEIVED SEPTEMBER 18,1930 PUBLISHED DECEMBER 18, 1930

The action of the Grignard reagent on certain alpha halo-ketones has been under investigation in this Laboratory in connection with the study of the coupling action of the Grignard reagent on certain types of halogen compounds.[1] The results obtained so far have been to some extent anticipated by Lowenbein and Schuster[2] in an article which has just appeared. For this reason our work, although not fully completed, is being reported in its present form.

In our work the original object in view was to extend if possible the coupling reaction to other types of active halogen compounds. Only the benzyl halides and their derivatives had been used in previous studies. Inasmuch as a-halo-ketones have a very reactive halogen atom, it seemed likely that the coupling reaction might take place when compounds of this type were treated with the Grignard reagent. Experiments with w-bromo-acetophenone showed that the great rapidity with which the carbonyl group was attacked by the Grignard reagent precluded the possibility of testing the behavior of the a-halogen atom toward this reagent. It was found possible, however, to get around this difficulty by introducing substituents into the two ortho positions, thus effectively inhibiting the tendency of the carbonyl group to undergo addition reactions. Further, in order to avoid the possibility of enolization, the a-hydrogen atoms were replaced by methyl groups. The compound eventually obtained which fulfilled all of these requirements was α-3,5-tribromo-2,4,6-trimethylisobutyrophenone (III).

This compound was prepared in two ways. The method first used involved the synthesis of α-bromo-2,4,6-trimethylisobutyrophenone (I) from mesitylene and a-bromoisobutyryl chloride by use of the method of Friedel and Crafts. The monobromo compound was low-melting and for this reason difficult to study. Its dinitro derivative (II) was prepared as a check on the structure. By direct bromination of I was obtained the tribromo compound (III) which was used in the Grignard study. This compound was prepared more advantageously from isobutyrylmesitylene (IV) by direct bromination.

When this a-bromo ketone was treated with methylmagnesium chloride or ethylmagnesium bromide neither coupling nor alkylation was observed.

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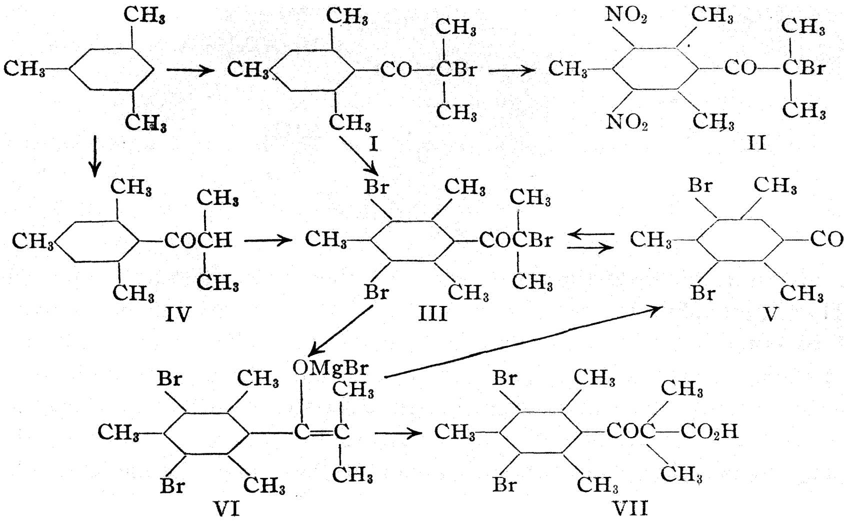
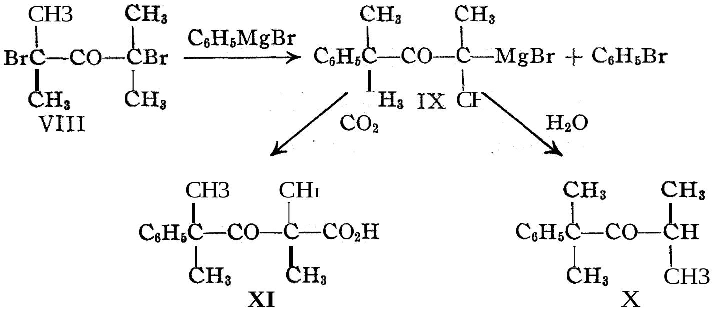
[1] For earlier papers in this field see Fuson, THIS JOURNAL, 48, 830, 2681, 2937 (1926).

[2] Lowenbein and Schuster, Ann., 481, 106 (1930).

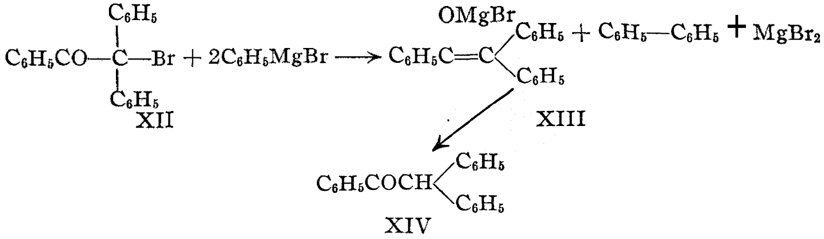


Instead the bromine was smoothly replaced by hydrogen. This result resembles that obtained by Umnova[3] who showed that when α,α'-dibromoisobutyrone (VIII) was treated with phenylmagnesium bromide there resulted a Grignard reagent having the formula IX. The simultaneous production of bromobenzene seems to establish this reaction as one of alkylation and radical interchange. The structure of IX was assigned on the basis of its reaction with water and with carbon dioxide* followed by water. In the first case the product was α-phenylisobutyrone (X) and in the second, α,α,γ-trimethyl-γ-phenyl-β-keto-valeric acid (XI).



Lowenbein and Schuster, in the investigation mentioned above, worked with benzoyldiphenylmethyl bromide (XII). With phenylmagnesium bromide this compound reacted to give diphenyl and the bromomagnesium enolate of triphenylethanone (XIII). The last-named compound when treated with water gave triphenylethanone (XIV).

[3] **Umnova,** *J. Russ. Phys.-Chem. Soc.*, 45,881 (1913).



It will be noted that these authors write their intermediate compound (XIII) as an enolate instead of as a true Grignard reagent such as Umnova used to explain the reaction with carbon dioxide (IX). Our results in the present work with α,3,5-tribromo-2,4,6-trimethylisobutyrophenone seem to parallel those of Lowenbein and Schuster rather than those of Umnova. When treated with methylmagnesium chloride or with ethylmagnesium bromide, the tribromo compound (III) gave the enolate, VI. This when treated with water gave 3,5-dibromo-2,4,6-trimethylisobutyrophenone (V). The structure of V follows from the fact that bromination converted it into α,3,5-tribromo-2,4,6-trimethylisobutyrophenone, from which it could be regained by reduction with zinc dust. Treatment with carbon dioxide, however, failed to convert VI into α,α-dimethyl-β-keto-β-(2,4,6-trimethyl-3,5-dibromophenyl)-propionic acid (VII). The reaction of our intermediate compound (VI) with benzoyl chloride, carbon dioxide and other typical reagents for the detection of the Grignard reagent is being further investigated.

Experimental Part

a-Bromoisobutyrylmesitylene (I).—A mixture of 50 g. (0.22 mole) of a-bromoisobutyryl bromide, 26 g. (0.22 mole) of mesitylene and 170 g. of carbon disulfide was placed in a 500-cc. three-necked flask equipped with a mercury-sealed stirrer and a reflux condenser with a tube to carry off the evolved hydrogen chloride. Through the remaining side neck of the flask was added in small portions over a period of one and one-half hours 40 g. of anhydrous aluminum chloride. The reaction flask was kept in an ice-water bath and the stirring was continuous throughout the period of addition of the aluminum chloride and for an hour afterward. A dark red color developed during the addition; this color gradually faded to a light red toward the end of the reaction.

The product was poured on cracked ice and a vigorous reaction took place. The crude product when distilled came over at 145–175° at 24 mm. Redistillation gave 41 g. of a golden-brown oil boiling at 160–170° at 24 mm. The yield was 69.5% of the theoretical. On long standing the oil deposited crystals of the α-bromoisobutyryl mesitylene, melting at 27°.

Anal. Calcd. for $C_{13}H_{17}OBr$: Br, 29.79. Found: Br, 29.22.

α,3,5-Tribromo-2,4,6-trimethylisobutyrophenone (III).—The a-bromoisobutyrylmesitylene described above was brominated by treatment with bromine in ice water. The oil boiling at 160–170° at 24 mm. was covered by a layer of water and cracked ice and an excess of bromine was added. During the addition of the bromine the mixture was shaken vigorously. The oil became very viscous and finally set to a solid. This was treated with a solution of sodium bisulfite to remove excess bromine. The product crystallized from 95% alcohol in colorless needles melting at 106–107° (corr.). The yield was nearly quantitative.

Anal. Calcd. for $C_{13}H_{15}OBr_3$: Br, 56.2. Found: Br, 56.1.

α-Bromo-3,5-dinitro-2,4,6-trimethylisobutyrophenone (II).—Four and one-half grams of a-bromoisobutyryl mesitylene was added slowly with agitation to a mixture of 10 cc. of concentrated nitric acid and 15 cc. of concentrated sulfuric acid. The temperature rose but was kept below 60° by immersion of the container in cold water. On standing for fifteen minutes the emulsion which had formed separated into two layers; the upper layer was orange in color and contained a finely divided solid, The reaction mixture was poured into cold water; a white solid came out. Thick needles melting at 117.8–118.5° were obtained after several recrystallizations from alcohol.

Anal. Calcd. for $C_{13}H_{15}O_5BrN_2$: Br, 22.3. Found: Br, 22.4.

α,3,5-Tribromo-2,4,6-trimethylisobutyrophenone (III) (Second **Method).**—It was found that this preparation could be carried out more conveniently by direct bromination of isobutyrylmesitylene. The procedure used was essentially that described in the preparation by the first method. A mixture of the products from the two sources showed no depression of the melting point.

The Action of **Methylmagnesium** Chloride on **α,3,5-Tribromo-2,4,6-trimethyliso**-butpophenone.—A solution of 9 5 g. (0.022 mole) of the tribromo ketone in 125 cc. of ether was added dropwise and with stirring (mercury-sealed stirrer) to a three-fold excess of the Grignard reagent contained in a three-necked flask. During the addition, which required about thirty minutes, the reaction mixture boiled gently without external heating. When the addition was complete the stirring and refluxing (from external heat) were continued for two and one-half hours. Cold dilute hydrochloric acid was added; this caused violent refluxing if added rapidly. The clear, colorless ether layer was washed twice with water and the ether carried off by a stream of air, leaving a white solid. All of the solid dissolved in hot 70% alcohol. On cooling the solution deposited a crystalline solid which melted at 62–64". Further recrystallization from methyl alcohol changed the melting point to 70–71° (corr.). This product was found to be 3,5-dibromo-2,4,6-trimethylisobutyrophenone (IV) by the reaction described below. The yield was 5.5 g. or 71% of the theoretical.

3,5-Dibromo-2,4,6-trimethylisobutyrophenone.—Five-tenths gram of the pulverized product and an excess of bromine were intimately mixed in a test-tube cooled by an ice–salt mixture. After ten minutes a solution of sodium bisulfite was added to remove excess bromine. After one recrystallization from alcohol 0.6 g. of a solid melting at 102–104.5" was obtained. This was shown to be α,3,5-tribromo-2,4,6-trimethylisobutyrophenone by the method of mixed melting points

Anal. Calcd. for $C_{12}H_{16}OBr_2$: Br, 46.0. Found: Br, 45.7

Reduction of α,3,5-Tribromo-2,4,6-trimethylisobutyrophenone with Zinc and Acetic Acid.—The method used was similar to that which Stephen and Weizmann[4] used to reduce ω-chloro-2,4-dihydroxy-acetophenone. One and one-half grams of the tribromo ketone, 4 cc. of glacial acetic acid, 16 cc. of water, and 100 cc. of 95% ethyl alcohol were placed in a 200-cc. flask fitted with a reflux condenser, and the temperature of the water-bath surrounding the flask was brought to 60°. Five grams of zinc dust was added and the temperature of the water-bath maintained at 60° for one hour, when 16 cc. of water and 4 cc. of acetic acid were again added. The temperature was kept at 60° for five additional hours.

The zinc dust was filtered, part of the solvent evaporated and water added, which

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[4] Stephen and Weizmann, J. Chem. *Soc.*, **105,** 1050 (1914).

caused the precipitation of a fine white solid. Two extractions with ether were made and the ether was allowed to evaporate. The residue after several recrystallizations from methyl alcohol melted at 69–70°. This was shown to be 3,5-dibromo-2,4,6-trimethylisobutyrophenone by the method of mixed melting points.

The Action of Ethylmagnesium Bromide on α,3,5-Tribromo-2,4,6-trimethylisobutyrophenone.—Several experiments similar to that described for methylmagnesium chloride were run with ethylmagnesium bromide. The tribromo compound was in all cases smoothly converted into the dibromo compound. In two runs the reaction mixture was treated for long intervals with carbon dioxide before being decomposed with water. The product was the same as in those runs in which no carbon dioxide was used. No acid could be isolated in any case.

Summary

α,3,5-Tribromo-2,4,6-trimethylisobutyrophenone (III) has been prepared by the bromination of isobutyrylmesitylene (IV) and of α-bromoisobutyrylmesitylene (I).

Treatment with methylmagnesium chloride or ethylmagnesium bromide transformed the tribromo compound (III) into an enolate (VI) which reacted with water to give 3,5-dibromo-2,4,6-trimethylisobutyrophenone (V).

The structure of the dibromo compound (V) was proved by its synthesis from III by zinc reduction and by the fact that bromination reconverted it into the tribromo compound.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORIES, PICATINNY ARSENAL]

THE NITRATION OF SYM.-DIPHENYLETHANE[1,2]

BY WM. H. RINKENBACH[3] AND H. A. AARONSON[4]

RECEIVED SEPTEMBER 19, 1930 PUBLISHED DECEMBER 18, 1930

Although various workers have reported the preparation and properties of a number of nitro derivatives of symmetrical diphenylethane (dibenzyl), it was considered advisable to carry out a more thorough investigation of the nitration of this compound. The object of this study was to determine the practicability of preparing the symmetrical hexanitro derivative by direct nitration, although it was considered probable that steric hindrance would prevent the formation of a high yield of hexanitrodiphenylethane.

Several dinitrodiphenylethanes are recorded in the literature, the 4,4′-dinitro compound being the most important. Stelling and Fittig[5] prepared this compound by the direct nitration of diphenylethane with nitric acid (sp. gr. 1.52) and reported the simultaneous formation of the 2,4′-

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[1] Published by permission of the Chief of Ordnance, U. S. War Department.

[2] Work undertaken at the suggestion of Mr. Lambert Thorpe.

[3] Chief Chemist, Picatinny Arsenal, U. S. War Department.

[4] Assoc. Organic Chemist, Picatinny Arsenal, U. S. War Department.

[5] Stelling and Fittig, Ann., 137, 260 (1866).

dinitro compound. It has been found possible to obtain 4,4'-dinitrodiphenylethane with a yield of 95% of the theoretical by the use of nitric acid having a specific gravity of only 1.42 according to the following procedure.

Thirty-five grams of diphenylethane was added to 105 g. of nitric acid (sp. gr. 1.42). There was no appreciable evolution of heat. The mixture was slowly heated and the temperature was maintained between 70 and 80° for six hours while being stirred. At the end of this time an oily layer below the spent acid was visible. After cooling, the mixture was drowned in ice water, filtered on a Büchner funnel and the retained nitro compound was washed thoroughly with water, air-dried and weighed; yield, 50.0 g. as compared with 52.5 g. calcd. This material was purified by repeated recrystallization from ethanol.

The pure 4,4'-dinitrodiphenylethane so obtained was in the form of light yellow needles which were found to melt at 180.5° (corr.). The melting point of this compound has been reported as being 178[6] 180–182[7] and 182°[8] by various workers, and particular care was taken in determining the above value with a thermometer calibrated by the U. S. Bureau of Standards.

Braun and Rawicz[9] reported the preparation of 2,4,2',4'-tetranitrodiphenylethane, obtaining a 70% yield of this compound when diphenylethane was added to ten times its weight of fuming nitric acid (sp. gr. 1.53) at −15°, allowing to stand at room temperature for one hour, and drowning in ice water. It was found possible to obtain 2,4,2',4'-tetranitrodiphenylethane with a yield of 90 to 95% by the use of the following procedure: 50 g. of diphenylethane was added slowly to 500 g. of fuming nitric acid (95%) which was stirred continuously and maintained at a temperature lower than 30°. When the mixing was complete the temperature was slowly raised to about 70° in the course of two and one-half hours, and maintained at this point for four hours. After cooling and standing overnight, heating at 70° was continued for two hours. Stirring was continued for two hours during cooling. The mixture was then drowned in ice water and filtered through a Büchner funnel. The retained solid was washed thoroughly with water to remove acid and with alcohol to remove any unnitrated diphenylethane. air-dried and found to weigh 91 g. Repeated recrystallizations of this material from benzene and toluene yielded pale yellow needles.

The pure compound so prepared was found to melt at 170.9° (corr.) as compared with the value 168–169° reported by Braun and Rawicz. It is insoluble in hot or cold ethanol, slightly soluble in ether or chloroform and appreciably soluble in hot benzene, toluene, acetone, acetic acid, ethylene dichloride or acetylene tetrachloride. It is nonhygroscopic and explodes in five seconds when heated at 380°. In spite of this, the compound is not detonated by the impact of a 2 kg. weight falling 34 inches; nor is it detonated by 0.4 g. of mercury fulminate or by 0.4 g. of tetryl with 0.23 g. of mercury fulminate in the sand test. However, when 0.40 g. of cyclotrimethylenetrinitramine with 0.23 g. of mercury fulminate is used, detonation takes place and the tetranitrodiphenylethane is found to crush 21 g. of sand as compared with 30 g. crushed by the same weight of trinitrotoluene.

Several attempts to prepare 2,4,2',4'-tetranitrodiphenylethane by the use of mixtures of sulfuric and nitric acids gave negative results. The diphenylethane was dissolved in 95% or in fuming (103%) sulfuric acid by heating to 110° and, after cooling,

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[6] Leppert, Ber., 9, 15 (1876)

[7] Green, Davies and Horsfall, J. Chem. *Soc.*, 91, 2079 (1907).

[8] W. Will, *Ber.*, 47, 704 (1914).

[9] Braun and Rawicz, *ibid.*, 49, 802 (1916).

a mixture of 95% sulfuric and fuming nitric (95%) acids or of fuming sulfuric and fuming nitric acids was added. After heating at 80 to 100° for from two to four hours, the mixture was cooled and drowned in ice water. Very little separation of solid material resulted and only a small quantity of the tetranitro compound was recovered. Only traces of other compounds were obtained by extracting the water solutions with organic solvents, neutralizing with sodium carbonate and extracting again. It would appear that the use of mixed acids for nitration results in almost complete decomposition of the diphenylethane.

The only reference to a nitro derivative of diphenylethane higher than the tetranitro compound found in the literature is a statement by Will[8] that 2,4,6,2',4',6'-hexanitrodiphenylethane is readily formed by the nitration of the dinitro compound and can also be prepared by the oxidation of 2,4,6-trinitrotoluene in the presence of alkalies. He gave no details of either method, but gave the melting point of the hexanitro compound as 212°.

Further nitration of tetranitrodiphenylethane by the use of fuming nitric acid or mixtures of fuming nitric and sulfuric acids caused no additional nitration, the unchanged tetranitro compound being recovered in each case. A number of attempts to prepare the hexanitro compound by the oxidation of trinitrotoluene in the presence of alkalies, using the method of Green, Davies and Horsfall,[7] gave negative results, even with the addition of ammonium persulfate to the solution. An effort to replace one or more hydrogen atoms of the methylene groups with the nitrate group was made, using the method of Walther and Wetzlich.[10] These workers found that hydrobenzoin dinitrate was formed by boiling diphenylethane with silver nitrate in glacial acetic acid; but when 2,4,2',4'-tetranitrodiphenylethane was substituted for diphenylethane in this procedure, only the unchanged tetranitro compound was recovered.

It was considered possible that a preliminary sulfonation of tetranitrodiphenylethane over an extended period might render nitration possible. A new compound was prepared by the following procedure: 142 g. of tetranitrodiphenylethane was added to 100 g. of fuming sulfuric acid (103%), and the temperature was maintained at 85° for four days. After cooling, 500 g. of fuming nitric acid (95%) was added, and the temperature was slowly raised to 85°. This temperature was maintained for two days, and the mixture was then cooled and drowned in ice water. The separated solid was caught on a Büchner funnel, washed thoroughly with water and air-dried. The weight was found to be 100 g.

On recrystallizing from toluene, the solution became black and the deposited crystals were contaminated with a dark material. Washing with alcohol and with ether removed this and when the alcohol and ether solution was evaporated to dryness, a few grams of a black, gummy residue was obtained. Repeated recrystallization of the crystalline material from toluene gave a pure product consisting of fine, pale cream-colored needles which melted at 187.3'.

Because of the melting point, the material prepared as described above was thought to be a new compound, and investigation showed it to be α-2,4,5-trinitrophenyl-β-2,4-dintrophenylhydroxyethane. The constitution of the compound was established by analysis.

Anal. Calcd.: C, 39.38; H, 2.14; N, 16.56. Found: C, 39.58; H, 2.38; N, 16.56.

From these results the empirical formula $C_{14}H_{10}N_5O_{11}$ was calculated, while that of the pentanitrohydroxy compound is $C_{14}H_9N_5O_{11}$. Since the empirical formula of the tetranitro compound is $C_{14}H_{10}N_4O_8$, it appeared probable that the new compound contained only nine hydrogen atoms, since

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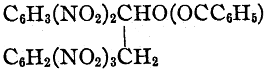
[10] Walther and Wetzlich, J. *prakt. Chem.*, 61, 174 (1854).

one nitrogen and three oxygen atoms had been added. The value found by the determination of hydrogen is believed to be high because of the difficulty in obtaining accurate results with so small a percentage present, but is within the experimental error. If this is granted, it is apparent that either a nitrate (NO_3) group has replaced one of the hydrogen atoms of the ethylene linkage, or a nitro (NO_2) group has replaced a hydrogen atom in one of the benzene rings and an oxygen atom has been added to the ethylene linkage or formed a phenol derivative.

Molecular weight determinations, with trinitrotoluene as the solvent, gave values of 417 and 427 (av., 422) as compared with 423 for α-2,4,5-trinitrophenyl-β-2,4-dinitrophenylhydroxyethane and 407 for pentanitrodiphenylethane. This confirms the presence of eleven oxygen atoms instead of the ten required for a pentanitro derivative.

A diphenylamine–sulfuric acid test for the presence of a side-chain nitrate or nitrite group gave a negative result. The sodium hydroxide test for a phenolic group[u] also gave a negative result. These results indicate that a nitro group has been substituted in one of the benzene rings and that the additional oxygen is attached to the ethylene linkage, probably to form a –CHOH– group.

The presence of a non-phenolic hydroxyl group was confirmed by treatment with benzoyl chloride in pyridine solution. A brownish powder melting at about 200° with decomposition was obtained. This was found to have a nitrogen content of 13.68% as compared with a theoretical value of 13.3% for



$$\begin{array}{l} C_6H_3(NO_2)_2CHO(OCC_6H_5) \\ \qquad\qquad\quad | \\ C_6H_2(NO_2)_3CH_2 \end{array}$$

These results indicate that two nitro groups are attached to one benzene ring, three to the other, and that one of the CH_2 groups had been oxidized to a CHOH group. The problem of determining the position of the third nitro group in one benzene ring and the position of the CHOH group with reference to the trinitrophenyl group was attacked as follows.

A portion of the pentanitrohydroxy compound was placed in a solution of chromic oxide in glacial acetic acid and the solution was boiled under a reflux condenser for sixty-two hours. After cooling, two compounds were isolated. One was slightly contaminated with the second, but melted at 188° and had a nitrogen content of 16.08%. This is believed to be sufficient identification as 2,4,5-trinitrobenzoic acid, which melts at 190–191° and has a nitrogen content of 16.35%.

The second compound did not melt even when heated to 275° and contained 11.16% of nitrogen. That it was an acetic ester was shown by hydrolyzing it with sulfuric acid in the presence of ethanol, when ethyl acetate was formed. This indicates that this compound has the constitution $C_6H_3(NO_2)_2CH(OOCCH_3)$, the theoretical nitrogen content of which is 11.72%.

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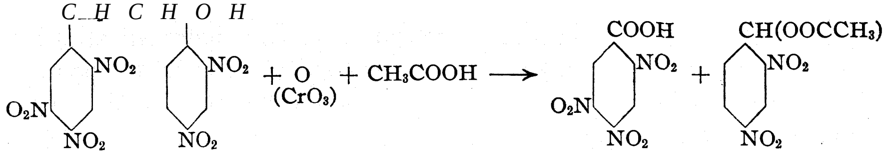
[11] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, Vol. I, p. **87.**

The foregoing facts indicate that the compound under investigation is α-2,4,5-trinitrophenyl-β-2,4-dinitrophenyl-hydroxyethane and that treatment with chromic oxide and glacial acetic acid gave rise to the reaction



This compound is very slightly soluble in alcohol or ether, but is appreciably soluble in hot benzene, toluene, acetone, ethylene dichloride or acetylene tetrachloride. When heated at 360°, it explodes in five seconds and explodes when subjected to the impact of a 2-kilogram weight falling 18 inches or more. It cannot be detonated by 0.4 g. of mercury fulminate, but when initiated with 0.25 g. of tetryl and 0.25 g. of mercury fulminate in the sand test, it crushes 21 g. of sand.

The formation of α-2,4,5-trinitrophenyl-β-2,4-dinitrophenylhydroxyethane is of unusual interest, as the direct effects of steric hindrance are easily recognizable. It is thought probable that prolonged sulfonation does no more than serve to introduce a nitro group in the 5-position instead of the 6-position normally substituted in the trinitration of monoalkylbenzene compounds. The introduction of the nitro group in the 5-position prevents oxidation of the adjacent β-methylene. The oxidation of the methylene group is evidently limited to one stage by the steric hindrance effect of the nitro groups already present in the compound and evidently is subsequent to the introduction of one of the nitro groups; otherwise both methylene groups would be oxidized and no nitration would take place, as the introduction of a third nitro group is more difficult than the oxidation of a methylene group.

The limitation of oxidation as an effect of steric hindrance is confirmed by results obtained in efforts to condense two molecules of α-2,4,5-trinitrophenyl-β-dinitrophenylhydroxy-ethane with the elimination of one molecule of water from the two hydroxyl groups. When the compound was dissolved in and heated with 95% sulfuric acid or a mixture of fuming sulfuric acid and phosphorus pentoxide, the unchanged compound was recovered. As such condensations are relatively easy when less complex hydroxy compounds are used, and the 2,4-dinitro compound recovered on splitting with chromic oxide was esterified by the glacial acetic present, the inhibitive effect of steric hindrance in α-2,4,5-trinitrophenyl-β-2,4-dinitrophenylhydroxyethane is great, although the preparation of a benzoate was not difficult.

In the course of this study, the pentanitrohydroxy compound was prepared several times. From the products of nitration in one case, using 140 g, of tetranitrodiphenylethane, there was isolated about 0.5 g. of a compound melting at 209°, and having a nitrogen content of 18.48%. This is undoubtedly the symmetrical hexanitrodiphenylethane mentioned by Will[5] as melting at 212° (18.59% N). In spite of repeated attempts to prepare more of this material, none was obtained. It is apparent that this compound is formed in very small amount under even the most favorable conditions.

Summary

1. Modified methods of preparing 4,4′-dinitro- and 2,4,2′,4′-tetranitrodiphenylethane with high yields have been developed. Accurate melting point determinations of these pure compounds, as well as other properties, have been recorded.

2. A new compound has been prepared by the nitration of tetranitrodiphenylethane and identified as α-2,4,5-trinitro-phenyl-β-2,4-dinitrophenylhydroxyethane. The important properties of this compound have been determined.

3. 2,4,6,2′,4′,6′-Hexanitrodiphenylethane is formed in very small amount under even the most favorable conditions of nitration.

4. The effects of steric hindrance in the formation of nitro derivatives of diphenylethane have been evaluated.

DOVER, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

MAGNESIUM DIALKYLS. AN HISTORICAL NOTE ON THE FIRST PREPARATION OF AN ALKYLMAGNESIUM HALIDE

BY HENRY GILMAN AND ROBERT E. BROWN

RECEIVED SEPTEMBER 19, 1930 PUBLISHED DECEMBER 18, 1930

Introduction

In extension of studies concerned with the preparation of phenylmagnesium chloride in the absence of a solvent,[1] some apparently anomalous reactions were observed when alkyl halides were heated with magnesium. This necessitated an investigation of the related magnesium dialkyls.

Hallwachs and Schafarik[2] were the first to prepare an organomagnesium compound, and this they did by heating ethyl iodide with magnesium. The solid reaction product when heated gave a colorless, volatile liquid which they said contained traces of the magnesium diethyl. Then Cahours,[3] by a like reaction, obtained an entirely volatile product which he considered magnesium diethyl. At a much later time, Lohr[4]

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[1] Gilman and Brown, THIS JOURNAL, 52, 3330 (1930).

[2] Hallwachs and Schafarik, *Ann.*, 109, 206 (1859).

[3] Cahours, *ibid.*, 114, 227, 240 (1860).

[4] Löhr, *ibid.*, 261, 48, 72 (1891). *See*, also, Fleck, *ibid.*, 276, 129 (1893), who used the mercury diethyl method of preparation described by Lohr. Extensive studies on the direct action of RX compounds and magnesium have been made by Spencer and co-workers, J. Chem. *Soc.*, 93.68, 1821 (1908).

prepared magnesium diethyl by heating ethyl iodide with magnesium and also by heating mercury diethyl with magnesium. In both cases the product was a non-volatile solid. This was subsequently confirmed? and then it was shown, incidental to other studies, that magnesium dimethyl[6] and magnesium di-n-butyl[7] were solids. There is a possibility that some higher, possibly branched-chain magnesium dialkyls might be liquids because although beryllium dimethyl is a solid, beryllium di-n-butyl is a liquid.[8]

Strictly speaking, the known magnesium dialkyls are volatile to a certain extent, for recent studies[9] have shown that these organomagnesium compounds can not only be sublimed in a high vacuum but also distilled in a stream of ether. Furthermore, the earlier literature[10] on these studies is incorrect in describing the magnesium dialkyls as being essentially insoluble in ether. They are distinctly soluble in ether. Possibly the higher magnesium dialkyls might be found to be sparingly soluble in ether, which is the case with magnesium diphenyl.[11] Other general observations on magnesium dialkyls are contained in the Experimental Part.

Undoubtedly Hallwachs and Schafarik[2] were the first to prepare an organomagnesium compound.[12] They may have been the first to prepare a so-called "individual" or ether-free organomagnesium halide, because either one, or both, of the following reactions can be used to account for their product.

$$2C_2H_5I + 2Mg \longrightarrow (C_2H_5)_2Mg + MgI_2 \qquad (I)$$

$$C_2H_5I + Mg \longrightarrow C_2H_5MgI \qquad (II)$$

There is not now[13] available a reaction for differentiating between ($R_2Mg + MgX_2$) and RMgX. Once the reaction product is dissolved, in a solvent such as ether, then the following equilibrium occurs.[14]

$$2C_2H_5MgI \rightleftharpoons (C_2H_5)_2Mg + MgI_2 \qquad (III)$$

In view of this equilibrium it is inconsequential whether Reaction I or Reaction II occurred, because in either case the equivalent of ethylmagnesium iodide is obtained.[15]

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[5] Gilman and Schulze, This Journal, 49, 2328 (1927).

[6] Gilman and Brown, *Rec. trav. chim.*, 48, 1133 (1929).

[7] Gilman and Brown, *ibid.*, 49, 724 (1930).

[8] Gilman and Schulze, J. *Chem. Soc.*, 2663 (1927).

[9] Gilman and Brown, This Journal, 52, 4480 (1930).

[10] Jolibois, Compt. *rend.*, 155, 353 (1912), who prepared magnesium diethyl in accordance with Lohr's directions from mercury diethyl, described his compound as insoluble in ether but soluble in an ethereal solution of magnesium iodide.

[11] Hilpert and Griittner, *Ber.*, 46, 1675 (1913). Gilman and Brown, *Rec. trav. chim.*, *49*, *202* (1930).

[12] We refer here not to carbides or to acetylides, but only to those types having an alkyl or aryl group attached directly to magnesium.

[13] Gilman and Brown, This Journal, 52, 1181 (1930). This refers to ether solutions. An x-ray investigation of the crystal structure of these two types should prove of assistance in differentiation.

[14] Leading references to related studies may be traced back from a recent article by Gilman and St. John, *ibid.*, 52, 5017 (1930).

[15] It is interesting to note that it was about forty years later that Grignard first

With the application of heat, the condition used in most of these preparations, the RMgX compound might have formed first and then have been converted to the R_2Mg compound, in accordance with Reaction III. It is known that such a transformation does occur on heating.[6,16] Also, it has been generally assumed that in the formation of other organometallic compounds, the organometallic halide (RMeX) is first formed and then is converted to the organometallic compound (R_2Me): as, for example, in the formation of zinc diethyl from ethyl iodide and zinc through the ethyl zinc iodide stage.

Even though the equilibrium pictured in Reaction III probably applies to a great many, if not all, organometallic combinations it is not necessary to assume that the first stage in the formation of an R_2Metal compound is the RMetalX type. The reaction might occur as follows, using magnesium as the metal.[17]

$$2RX + Mg \longrightarrow 2R- + MgX_2 \qquad (IV)$$

$$2R- + Mg \longrightarrow R_2Mg \qquad (V)$$

Previously, it was assumed that RMgX or ($R_2Mg + MgX_2$) compounds were formed as follows:

$$RX + Mg \longrightarrow R- + -MgX \qquad (VI)$$

$$R- + -MgX \longrightarrow RMgX \qquad (VII)$$

This latter interpretation has some objections,[17] not the least of which is its lack of comprehensiveness, as in a reaction between mercury diethyl and a metal, where no halogen is present. Admittedly, both types of reaction might take place concurrently.

Experimental Part

The technique employed was that described earlier[1] in the preparation of phenylmagnesium chloride, a water pump being used to evacuate the tubes prior to sealing at the vapor pressure of the liquid. The magnesium was freshly ground and of 30-80 mesh. The qualitative color test, quantitative acid titration and characteristic derivatives were those used in other related studies in this Laboratory.

Methyl iodide showed no reaction even after heating at 140–150° for twelve hours. We have no explanation for the vigorous reaction reported by Cahours.[3] However, because he describes his magnesium dimethyl as a volatile, inflammable liquid, we are inclined to the opinion that his magnesium might have contained significant quantities of metallic impurities, such as zinc.

Ethyl iodide reacts at room temperatures, and the yield of organometallic compound at the end of seven days was 46%. When one equivalent of ethyl iodide was heated at 120–130° for four hours with two equivalents of magnesium, the yield was 61%. When two equivalents of ethyl iodide are used with one equivalent of magnesium no

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prepared ether solutions of RMgX compounds. But it was just this operation of Grignard in preparing the RMgX compounds in ether which made it possible for these reagents to find their wide application.

[16] Giman and Fothergill, THIS JOURNAL, 51, 3149 (1929).

[17] This interpretation is developed in a paper by Gilman and Brown, Rec. *trav. chim.*, 49 (1930).

organometallic compound results. This is undoubtedly due to a secondary reaction between ethylmagnesium iodide or magnesium diethyl and the excess of ethyl iodide.

n-Butyl iodide appears to react more readily than ethyl iodide at room temperature. It is interesting to note that so far we have obtained no reaction under moderate conditions between trimethylene chloro-iodide, $ClCH_2CH_2CH_2I$, and magnesium.

Ethyl bromide did not react at room temperatures in seven days. When heated at 120–130° for four hours a reaction occurred with the formation of magnesium bromide and gaseous products, but no color test was obtained. Very probably an organometallic compound will be obtained from ethyl bromide under intermediate conditions. Essentially the same results were obtained with n-butyl chloride and n-butyl bromide

Methyl[18] and ethyl acetates have pronounced catalytic effects in initiating reaction, particularly with an iodide like ethyl iodide. They have practically no effect with methyl iodide.

Magnesium diethyl and magnesium di-n-butyl are very soluble in ether. Magnesium dimethyl is somewhat less soluble than the other two magnesium dialkyls, and a solution of it in ether contained in a sealed tube, deposited fine needle crystals after about six months' standing. The approximate solubility of magnesium dimethyl in ether is 0.08 mole per 100 cc. of solvent. These crystals of magnesium dimethyl (or its etherate) are markedly similar in appearance to the related beryllium dimethyl.8 The three magnesium dialkyls just described were prepared from the corresponding mercury dialkyls. The product obtained from ethyl iodide and magnesium is only slightly soluble in pure ethyl iodide.

In general, the organomagnesium compounds prepared from magnesium and a mercury dialkyl appear to be more reactive to atmospheric oxygen and moisture than the corresponding compounds prepared from magnesium and an alkyl iodide. Whenever the dry powders, prepared from the mercury dialkyls, are allowed to come in contact with water the mixture almost always takes fire. Ether solutions of the magnesium dialkyls take fire with water, but not so readily as the dry powders. The dry powders sometimes took fire in air, but no definite data are at hand because these compounds were always manipulated in an atmosphere of nitrogen or hydrogen. **A** high humidity was conducive to such combustion when the powders were exposed to the air.

Summary

A description is given of some general properties of magnesium dialkyls prepared from magnesium and mercury dialkyls, and organomagnesium compounds prepared from alkyl iodides and magnesium (with no solvent). The first organomagnesium halide, or its equivalent, was prepared by Hallwachs and Schafarik in 1859 in ***the absence of ether,*** but the use of ether by Grignard first made possible the extensive applications of these compounds.

AMES, IOWA

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[18] Methyl acetate was found by Renshaw and Greenlaw, THIS JOURNAL, 42, **1472** **(1920).** to be very effective in the preparation of zinc dimethyl.

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

THE SYNTHESIS OF GLUCOSIDOFERULIC ACID

BY RAYMOND M. HANN

RECEIVED SEPTEMBER 27, 1930 PUBLISHED DECEMBER 18, 1930

The natural occurrence of hydroxycinnamic acids and their internal lactones, the coumarins, in the free state and in glucosidic combinations has been demonstrated repeatedly. While ferulic acid (3-methoxy-4-hydroxycinnamic acid) has been observed in the free state by Ponti[1] in the extract from the macerated plants of *Ajuga iva*, the isolation of its glucoside does not seem to have been reported. Power and Tutin,[2] however, have shown it to be an integral portion of the chalcone, homoeriodictyol (2,4,6-trihydroxyphenyl-4-hydroxy-3-methoxystyryl ketone) in Eriodictyon *californicum*, and the occurrence of its related alcohol, coniferyl alcohol (3-methoxy-4-hydroxycinnamyl alcohol) in the glucoside coniferin is well known. The present communication describes the synthesis of ferulic acid d-glucoside. The procedure adopted in this study was that of the interaction of the sodium salt of the methyl ester of ferulic acid with acetobromoglucose in cold alcoholic solution. This plan materially shortened the usual method of agitation of an ether solution of the acetylated sugar halide with an alkaline aqueous solution of the phenolic acid ester. The resulting tetra-acetylglucosidoferulic acid methyl ester was simultaneously de-esterified and de-acetylated by treatment with cold barium hydroxide, yielding directly the desired glucosidoferulic acid, which was obtained in crystalline form. Its rotation shows it to be the β-glucoside, as would be expected from its synthesis from acetobromoglucose.

Experimental

Methyl Ferulate.—Ferulic acid was prepared by the Knoevenagel condensation of vanillin with malonic acid in the presence of pyridine and piperidine according to the directions of Robinson and Shinoda.[3] The acid (4 g.) was esterified by boiling for four hours under a reflux condenser with 25 cc. of absolute methyl alcohol and 1 cc. of concd. sulfuric acid. The oily ester was precipitated by addition of 75 cc. of water, then extracted with ether and the ether solution was washed with dilute sodium carbonate, dried over calcium chloride, and evaporated until free of ether. The oily ester (3.6 g. or 84% of the theoretical) was used directly in the condensation with acetobromoglucose.

Methyl Tetra-acetyl-β-*d*-glucosidoferulate (Methyl **3-Methoxy-4-tetra-acetylglucosido-cinnamate).**—A solution of 3.4 g. of methyl ferulate in 25 cc. of absolute alcohol was treated with an amount of alcoholic potassium hydroxide (17.6 cc. containing 0.0517 g. per cc.) sufficient exactly to neutralize the phenolic hydroxyl. The solution was cooled in ice and an ether solution of 6.7 g. of acetobromoglucose rapidly added.

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[1] Ponti, *Gazz. chim. ital.*, **39**, II, 349 (1920).

[2] Power and Tutin, J. *Chem. Soc.*, 91, 887 (1907).

[3] Robinson and Shinoda, ibid., 127, 1973 (1925).

Following an immediate cloudiness a rapid precipitation of potassium bromide took place. Following a period of standing the salt was removed and the ether–alcohol solution evaporated to a sirup by an air current. Upon standing crystallization occurred, which was aided by cautious addition of 50% ethyl alcohol. The separated crystals were filtered off, washed and recrystallized from 50% ethyl alcohol; yield 5.6 g. (64% of the theoretical).

Methyl tetra-acetylglucosidoferulate separated from its solutions in 50% ethyl alcohol in colorless brilliant platelets, almost needle-like in character. It melts to a clear oil at 142–143° (corr.). A determination of its rotation in chloroform gave a value of $[\alpha]_D^{20}$ $-32.3°$ (0.2408 g. in 25 cc. of $CHCl_3$ solution gave a reading of 0.623° to the left in a 2-dm. tube). An acetyl determination by the method of Kunz[4] indicated that simultaneous de-acetylation and de-esterification took place (0.2304 g. substance consumed 10.8 cc. of $N/5$ NaOH; calcd., 10.7 cc.). A micro combustion was performed by Dr. R. T. K. Cornwell, to whom thanks are herewith expressed.

Anal. Subs., 3.943 mg.: CO_2, 8.095 mg.; H_2O, 1.943 mg. Calcd. for $C_{25}H_{30}O_{13}$: H, 5.62, C, 55.74. Found: C, 55.99; H, 5.51.

β-*d*-Glucosidoferulic Acid (3-Methoxy-4-β-d-glucosido-cinnamic Acid).—For saponification and de-acetylation of the tetra-acetylated methyl ester glucoside an aqueous 6% solution of barium hydroxide was used. Two grams of the finely powdered acetylated glucoside was shaken with 100 cc. of the alkali solution for eighteen hours, when solution was complete. The barium was precipitated successively as the carbonate and sulfate and the precipitate thoroughly extracted with boiling water. Upon concentrating the filtrate and washings under reduced pressure at 40° to a small volume, the glucoside of ferulic acid separated in colorless needles. It is almost insoluble in cold water. It was repeatedly recrystallized from boiling water for purification; yield, 1.1 g.

Glucosidoferulic acid crystallizes from boiling water, in which it is readily soluble, in colorless, brilliant, long, acicular needles containing one molecule of water of crystallization. This is retained at room temperature and ordinary humidity, but is rapidly lost over calcium chloride even at room temperature, the brilliancy of the crystal being replaced by a dull cottony appearance. Upon heating the glucosido acid in *vacuo* at 110° some loss of carbon dioxide occurs and at 180° an amount comparable to one molecule, although partial sublimation of the residue prevented an accurate determination. It is conceivable that the corresponding styrene derivative is formed as has been demonstrated in the case of caffeic acid (3,4 dihydroxycinnamic acid).[5]

The acid melts at 198–199° (corr.) without appreciable decomposition to a colorless oil. Its solutions rotate the plane of polarized light to the left, its $[\alpha]_D^{21}$ value being $-36.6°$ (0.2433 g. in 10 cc. of absolute alcohol solution gave a value of $-0.890°$ in a 1 dm. tube). A micro analysis was carried out.

Anal. Subs., 6.549 mg.: CO_2, 12.302 mg.; H_2O, 3.489 mg. Calcd. for $C_{16}H_{20}O_9 \cdot H_2O$: C, 51.31; H, 5.93. Found: C, 51.22; H, 5.96.

The writer takes this opportunity to express to Dr. C. S. Hudson his appreciation of the many kindnesses extended during the course of this research.

Summary

By the interaction of acetobromoglucose and the sodium salt of methyl ferulate, crystalline methyl ferulate β-*d*-glucoside-tetra-acetate has been

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[4] Kunz and Hudson, THIS JOURNAL, 48, 1982 (1926).

[5] Kunz-Krause, *Ber.*, 30, 1617 (1897).

synthesized. Through alkaline saponification it has been converted to crystalline β-*d*-glucosidoferulic acid, a glucoside which is closely related to the naturally occurring coniferin.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

THE TOXICITY OF ROTENONE, ISOROTENONE AND DIHYDROROTENONE TO GOLDFISH[1]

BY W. A. GERSDORFF

RECEIVED OCTOBER 2, 1930 PUBLISHED DECEMBER 18, 1930

The method used by the author for the study of toxicity in which the goldfish serves as the test animal has been described in a previous paper.[2] This method was used in studying the relative toxicities of rotenone, and two of its derivatives, isorotenone and dihydrorotenone. These substances were prepared by F. B. LaForge and L. E. Smith of this Division[3] in their researches to determine the chemical structure of rotenone.

The chemical structure of these compounds is not yet known. The empirical formula of rotenone is $C_{23}H_{22}O_6$. It possesses a ketone group, two methoxyl groups, a lactone group and an oxygen atom which is probably in the form of an ether linkage. LaForge and Smith reported that dihydrorotenone was one of the products of the catalytic reduction of rotenone, the reaction involving the simple reduction of an unsaturated bond in the rotenone molecule. It is now known that the double bond reduced is that in an isopropylene group. Isorotenone differs from rotenone in the position of its double bond. The double bond of the isopropylene group in rotenone has migrated and an isopropyl group has formed. The chemical relationship of these compounds will be discussed in a forthcoming paper by H. L. Haller of this Division.

The data are given in Tables I to III. The survival time curves and velocity of fatality curves which were plotted from these data are given in Figs. 1 to 3. In the former the ordinates are survival times in minutes; in the latter, the reciprocals of the survival times multiplied by 100. In both kinds of curves the abscissas are concentrations in milligrams per liter.

These curves resemble those given by Powers[4,5] to show the general type of toxic action to goldfish and that given by Carpenter[6] to show the

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[1] Presented as a part of the Insecticide Symposium before the Division of Agricultural and Food Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 7 to 11, 1930.

[2] W. A. Gersdorff, THIS JOURNAL, 52, 3440–3445 (1930).

[3] F. B. LaForge and L. E. Smith, *ibid.*, 51, 2574–2581 (1929).

[4] Edwin B. Powers, *Ill. Biol. Mono.*, 4, No. 2 (1917).

[5] Edwin B. Powers, *Ecology*, 1, 95–112 (1920).

[6] Kathleen E. Carpenter, *Brit. J. Exptl. Biol.*, 4, 378–390 (1927).

toxicity of sodium chloride to minnows (*Leuciscus phoxinus*). The toxic action does not, therefore, resemble that found by Powers in three anomalous cases in which cupric chloride, ferric chloride and cadmium chloride were the toxic substances nor that found by Carpenter in tests with soluble salts of heavy metals including the above three and lead, zinc and mercury. However, Carpenter found that these substances showed a similar

TABLE I

TOXICITY TO GOLDFISH OF ROTENONE AT 27.0 ± 0.2°

Concn., mg. per liter	No. of fishes used	Mean length of fishes, mm.	Mean weight of fishes,[a] g.	Mean surv. time, min.	Mean $\frac{100}{\text{surv. time}}$
4.0	4	40	2.0	46	2.19
3.0	3	37	1.6	46	2.16
2.0	4	37	1.6	48	2.08
1.0	4	39	1.8	49	2.06
0.90	7	38	1.7	52	1.91
.70	7	39	1.8	60	1.71
.50	8	39	1.8	57	1.82
.30	13	39	1.8	70	1.51
.20	16	38	1.7	65	1.55
.10	12	42	2.3	95	1.08
.075	10	43	2.4	115	0.87
.050	11	41	2.2	150	.70
.035	12	41	2.2	252	.42
.025	16	43	2.4	589	.23
.015	7	..	...	2400	.04

[a] Estimated from length.

TABLE II

TOXICITY TO GOLDFISH OF ISOROTENONE AT 27.0 ± 0.2°

Concn., mg. per liter	No. of fishes used	Mean length of fishes, mm.	Mean weight of fishes,[a] g.	Mean surv. time, min.	Mean $\frac{100}{\text{surv. time}}$
4.0	2	41	2.2	116	0.87
3.0	1	47	3.1	120	.83
2.0	6	41	2.2	132	.76
1.0	10	40	2.0	147	.69
0.80	8	41	2.2	153	.66
.50	11	43	2.4	155	.65
.30	7	42	2.3	148	.68
.25	10	41	2.2	162	.63
.20	13	40	2.0	197	.51
.15	12	44	2.6	226	.44
.10	17	43	2.4	396	.25
.090	1	..	...	470	.21
.070	2	43	2.4	730	.14
.060	1	..	...	1380	.07
.050	1	Still alive and apparently unaffected when taken out after 87 hours.			
.025	2				

[a] Estimated from length.

TABLE III

TOXICITY TO GOLDFISH OF DIHYDROROTENONE AT 27.0 ± 0.2°

Concn., mg. per liter	No. of fishes used	Mean length of fishes, mm.	Mean weight of fishes[a], g.	Mean surv. time. min.	Mean $\frac{100}{\text{surv. time}}$
1.0	4	44	2.6	75	1.36
0.50	8	43	2.5	74	1.38
.40	2	42	2.3	92	1.09
.25	12	42	2.3	96	1.09
.20	16	44	2.6	111	0.94
.15	13	41	2.2	121	.85
.10	14	40	2.1	128	.84
.080	13	40	2.1	132	.82
.050	21	39	1.9	158	.70
.040	12	37	1.7	174	.58
.030	14	40	2.1	280	.42
.015	6	40	2.1	720 ±	.17

[a] Estimated from length.

general type of effect which was marked by the formation of film over gills and skin and resulted in death by suffocation. When less than a certain amount of metallic ion was present the film was shed and complete recovery took place. In the tests with rotenone, isorotenone and dihydrorotenone no such film formation was apparent.

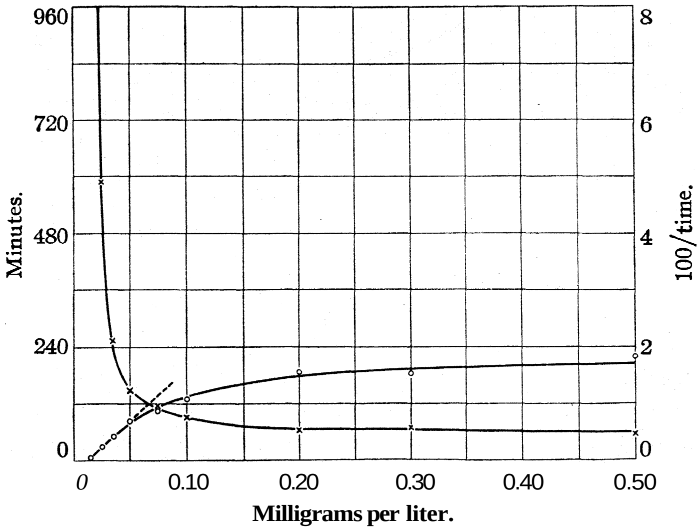

Fig. 1.—Toxicity curves for rotenone.

As Osterhout[7] pointed out, the values for the relative toxicities of substances will vary according to the criterion used. There are serious ob-

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[7] W. J. V. Osterhout, "The Measurement of Toxicity," J. Biol. Chem., 23, 26–70 (1915).

jections to the comparison of the survival times at a given concentration, to the comparison of the concentrations necessary to produce death (or any other phenomenon used as the criterion) in any arbitrarily fixed time, and to the comparison of the concentrations necessary to just cause death (threshold of toxicity concentration). These are easily seen in an inspection of the survival time curves. Limiting concentrations vary so that the relative toxicities of two substances, when compared by the first method, will change, depending on the concentration used. For example, as seen in the data, at 4 mg. per liter, rotenone is apparently two and one-half times as toxic as isorotenone; at 0.20 mg. it is three times, at 0.10 mg. four times and at 0.075 mg. nearly six times as toxic, whereas at 0.050 mg. its toxicity becomes indefinitely greater since at this concentration isorotenone is no longer toxic at all. Similarly, the relative toxic values vary when the concentrations necessary to kill in an arbitrarily chosen survival time are compared, and they become worthless if they are obtained from data falling on either that portion of the survival time curve approaching the horizontal or that portion approaching the vertical. If substances are compared by this single survival time method, this survival time should fall on the middle portion of the curve, that is, the portion that approaches an equilateral hyperbola. The third method, the comparison of the concentrations necessary to just cause death, involves the determination of values very difficult to obtain with precision and in addition deals only with one factor in toxicity, the threshold of toxicity. From the velocity of fatality curves it is seen that there are at least two variables in toxicity and these apparently vary independ-

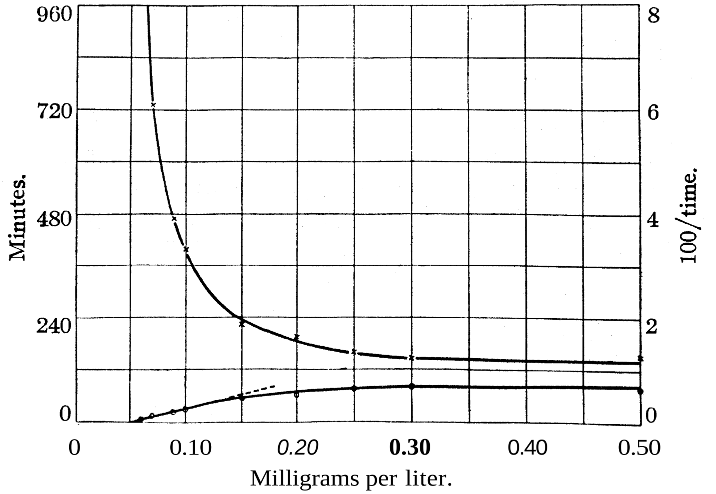

Fig. 2.—Toxicity curves for isorotenone.

ach other. They are the threshold of toxicity concentration te of increase of the velocity of fatality. Powers[4] adopts as a toxicity a value based on the reciprocal relation of these two 1 calculated from the equation, toxicity = $\sqrt{\tan \theta / a}$, where esents the slope of that portion of the velocity of fatality curve oaches a straight line and a its point of intersection, when proth the x-axis. Powers designated this straight line as the velocity of fatality curve and the concentration represented nt *a* as the theoretical threshold of toxicity concentration.

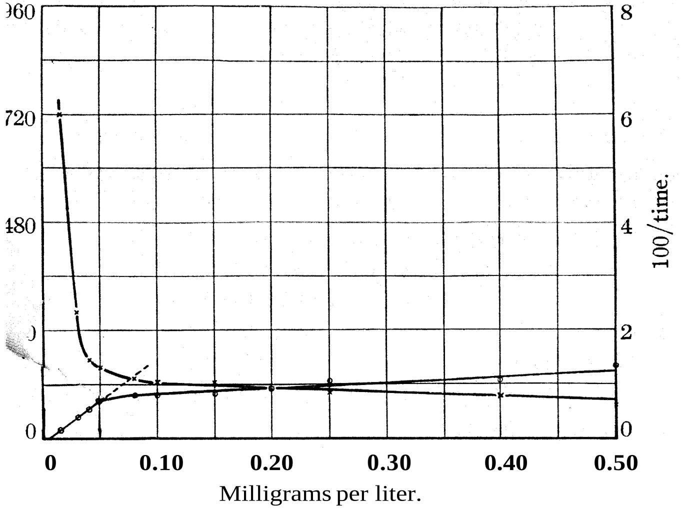

Fig. 3.—Toxicity curves for dihydrorotenone.

nparative toxicities of the substances considered here, derived to this equation, are shown in Table IV.

TABLE IV

'E TOXICITIES TO GOLDFISH OF ROTENONE, ISOROTENONE AND DIHYDRO-ROTENONE AT 27

Substance	a,[a] mg. per liter	Tan θ[b]	Toxicity $\sqrt{\frac{\tan \theta}{a}}$	Relative toxicity with respect to rotenone
enone	0.0125	0.187	3.9	1.0
otenone	.055	.053	1.0	0.26
ydrorotenone	.005	.156	5.6	1.4

ieoretical threshold of toxicity, *i. e.*, the concentration necessary to just kill.
ite of increase of the theoretical velocity of fatality with increase in concentra-
e values are based on the expression of concentration in milligrams per liter minutes.

1 appear from this study that this formula for toxicity is not all 1 be desired. Because the threshold of toxicity concentration

for dihydrorotenone is much smaller than that for rotenone, toxicity of the former is nearly half again as great as that Yet there is another variable which, if considered, would alt tive values and bring them closer together, a relationship after an inspection of the curves of the two substances. show that after reaching its maximum the rate of increase of of fatality with increase in concentration decreases much in dihydrorotenone than in rotenone. It is hoped that a for developed which will include this third factor. On the other not really be significant to express the toxicity of a substan value, but to define it according to the three variables, thresho rate of increase of the velocity of fatality and decrease of this

Conclusions

The toxicity of rotenone begins at a higher concentration dihydrorotenone (about twice, according to Powers' formula) concentration than that of isorotenone (about one-fourth). of rotenone and dihydrorotenone increase with increase in at about the same rate, but this rate is lower in the case (about one-third). At higher concentrations, rotenone is and isorotenone the least. According to Powers' formula expression of relative toxicity based on the first two variab stances have the following decreasing order of toxicity: dihy rotenone and isorotenone.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO STAT

THE RESOLUTION OF 1-(ALPHA-1-PIPERIDYLBE NAPHTHOL[1]

BY WALLACE R. BRODE AND JOSEPH B. LITTMAN

RECEIVED OCTOBER 2, 1930 PUBLISHED DECEMBER 18, 193

In a previous article on the condensation of secondary naphthols and aldehydes[2] a description was given of the pi 1-(α-1-piperidybenzyl)-2-naphthol. This asymmetric amine series of amines which are being prepared and tested as reso At the present time only one synthetic amine, namely, α- amine, has been used to any great extent for this work, most b agents being alkaloids, where only one of the two possible is available for use.

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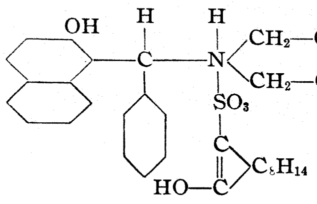
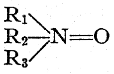
[1] An abstract of a portion of a thesis submitted by Joseph B. Litt fulfilment of the requirements for the degree of Doctor of Philosophy at University.

[2] Littman and Brode, THIS JOURNAL, 52, 1655 (1930).

dl-1-(α-1-Piperidylbenzyl)-2-naphthol can be resolved easily by means of d-camphorsulfonic acid. It has a high specific rotation, $[\alpha]_D$ −211°. Its use as a resolving agent, however, seems to be limited to strongly acidic compounds. Its solubility properties are poor for an ideal resolving agent but it does have acceptable qualities in its ease of crystallization, stability in the presence of common reagents and resistance to oxidation. In these latter qualities it is a marked improvement over the parent substance from which it is derived, 1-(α-aminobenzyl)-2-naphthol.[3,4]

From a comparison of the structural formula of 1-(α-1-piperidylbenzyl)-2-naphthol-d-camphorsulfonate (A) with the general formula of the amine oxides (B) which have been resolved by Meisenheimer,[5] it would appear


A


B

that there was a close relation in their configuration and one might possibly expect an asymmetric nitrogen atom in the first compound. Careful fractionation and a study of the rotation of various fractions failed to show any evidence of more than the two expected fractions in the resolution of a compound containing a single asymmetric atom. In similar attempts Barrowcliff and Ripping[6] did not succeed in resolving benzylmethylpiperidium-d-bromocamphorsulfonate and Wedekind[7] found it impossible to resolve quaternary ammonium bases with a double linking between carbon and nitrogen, ($Ph_2C{=}NMePhI$). In the case of the amine oxides, Meisenheimer[8] believes that the double bond between nitrogen and oxygen is semipolar, the oxygen atom figuring both as the fourth positive radical and taking the place of the negative ion of the ammonium salt.

Experimental

Thirty grams of *dl*-1-(α-1-piperidylbenzyl)-2-naphthol[2] was dissolved in 1300 cc. of absolute ethyl acetate on warming to 50°. To this solution, in a 2-liter round-bottomed flask, 22 g. of d-camphorsulfonic acid[9] dissolved in 200 cc. of absolute ethyl acetate was added. Soon after the addition of the d-camphorsulfonic acid solution, small colorless rosets began to form, which, after sixteen hours' standing, were filtered

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[3] Betti, Gazz. *chim. ital.*, **31**, I, 385 (1901).

[4] "Organic Syntheses," John Wiley and Sons, Inc., New York, **1929**, Vol. IX, p. 60.

[5] Meisenheimer, *Ber.*, **41**, 3966 (1908).

[6] Barrowcliff and Kipping, J. *Chem. Soc.*, 83, 1141 (1900).

[7] Wedekind, *Ann.*, **422**, 119 (1925).

[8] Meisenheimer, *ibid.*, 449, 188 (1926).

From the Eastman Kodak Co., $[\alpha]_D$ +20.98°.

and washed with hot ethyl acetate; yield, 28.5 g. (Fraction I), After eight more hours the filtrate yielded 7.7 g. of the salt, (Fraction II). The filtrate was evaporated to 850 cc. from which 4 g. of the salt was obtained (Fraction III).

The remaining filtrate was evaporated to dryness under reduced pressure, leaving a residue, somewhat yellow in color, which weighed 9.2 g. (Fraction IV). The total yield in all four fractions was 49.4 g. (theoretical, 51.9 g.).

Fraction I was recrystallized nine times by dissolving in 40 cc. of hot chloroform and then adding twice that volume of ethyl acetate. The degree of resolution and fractionation of the salts was followed by taking the optical rotation of the various fractions. The polarimetric observations were made on a Franz Schmidt and Haensch polarimeter, which was accurate to one hundredth of a degree rotation.

The salt, after the seventh, eighth and ninth recrystallization, had a constant rotation. 0.9385 g. made up to 10 cc. with chloroform at 20° gave $\alpha_D = +0.45°$; $l = 1$; $[\alpha]_D^{28}$ +4.7°. The salt from the ninth recrystallization, levo 1-(α-1-piperidylbenzyl)-2-naphthol-d-camphorsulfonate, melted with decomposition at 184–185° (corr.).

Anal. Calcd. for $C_{32}H_{39}O_5NS$: S, 5.82. Found: S, 5.79%.

Fractions II, III and IV were combined and fractionally recrystallized from a mixture of chloroform and ethyl acetate. The final mother liquor on evaporation gave a hard yellow mass which proved to be the dextro 1-(α-1-piperidylbenzyl)-2-naphthol-*d*-camphorsulfonate.

Preparation of the Free Amines.—Five grams of the levo 1-(α-1-piperidylbenzyl)-2-naphthol-d-camphorsulfonate was suspended in 50 cc. of water and to this suspension 100 cc. of 10% sodium carbonate solution was added. The mixture was poured into a separatory funnel and extracted thrice with 50-cc. portions of benzene. The benzene extracts were combined and dried with anhydrous sodium sulfate. The dried benzene solution was allowed to evaporate spontaneously in a beaker. The yield was 2.5 g. The levo-(α-1-piperidylbenzyl)-2-naphthol was recrystallized twice from a benzene-ligroin mixture, m. p. 201–202° (corr.).

Rotation. 0.2151 g. made up to 10 cc. with benzene at 20° gave $\alpha_D = -4.55$; $l = 1$; $[\alpha]_D^{27}$ −211°. 0.2036 g. made up to 10 cc. with chloroform at 20° gave $\alpha_D = -3.94$; $l = 1$; $[\alpha]_D^{28}$ −193°.

Three grams of the dextro salt was hydrolyzed with dilute sodium carbonate solution in the same manner as for the levo salt. The *d*-1-(α-1-piperdylbenzyl)-2-naphthol obtained was recrystallized twice from a benzene–ligroin mixture. The yield was 1.4 g., m. p. 199–200° (corr.).

Rotation. 0.2148 g. made up to 10 cc. with benzene at 20° gave $\alpha_D = +4.06$; $l = 1$; $[\alpha]_D^{31}$ +189°.

Summary

1-(α-1-Piperidylbenzyl)-2-naphthol has been resolved into its two active forms by means of d-camphorsulfonic acid.

COLUMBUS, OHIO

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

SOME ESTERS OF TRIBROMOMETHYLPHENYLCARBINOL

BY J. W. HOWARD

RECEIVED OCTOBER 11, 1930 PUBLISHED DECEMBER 18, 1930

Introduction

Tribromomethylphenylcarbinol was first prepared by Siegfried,[1] who gives no further experimental details than to state that he used the method of Jocitsch[2] to prepare the analogous chlorine compound. The author[3] has already submitted an improved method for the preparation of trichloromethylphenylcarbinol but now finds that that method must be further modified in order to isolate the analogous bromine compound, on account of its greater instability toward heat.

Siegfried prepared only the acetic ester of this carbinol, using acetyl chloride as the acetylating agent. In the present study acetic anhydride has been used. Corrected melting points of the carbinol and its acetic ester as well as other new data concerning these compounds are also submitted.

In addition, the propionic, butyric and benzoic esters have been prepared and studied.

Experimental Part

Preparation of Tribromomethylphenylcarbinol.—To a mixture of 37 g. of *freshly distilled* benzaldehyde and 130 g. of *dry* bromoform was added with constant stirring 4 g. of powdered potassium hydroxide over a half-hour period. The mixture was allowed to stand for two hours, ether was added and the resultant mixture filtered. The filtrate was distilled until the temperature reached 155° at 680 mm. It was then steam distilled to remove the remainder of the benzaldehyde and small amounts of benzoic acid. The residue was washed with dilute sodium bicarbonate solution, extracted with ether, dried over sodium sulfate and the ether distilled off. The liquid residue crystallized out in one to two days. These crystals were dried on *a* porous plate and recrystallized from 50% acetic acid. Small amounts of crude material can be recovered from the mother liquor by dilution. A yield of 16–18 g. of plate-like crystals melting at 72.5–73.0° was obtained.

Anal. Calcd. for $C_8H_7OBr_3$: Br, 66.81. Found: Br, 66.78.

This compound is only very slightly soluble in water but readily soluble in carbon bisulfide, ethyl alcohol, methyl alcohol, benzene, acetone, ether, chloroform and carbon tetrachloride.

Preparation of the Esters

The acetate and propionate were prepared by heating the carbinol with the corresponding anhydrides at 130–135° for three hours. Both readily formed plate-like crystals on pouring the reaction mixture into water. The acetate was recrystallized from 50% alcohol and the propionate from 75% acetic acid; m. p. of acetate, 133°.

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[1] Siegfried, *Chem. Centr.*, 1, 606 (1899).

[2] Jocitsch, *ibid.*, [5] 1, 1013 (1897).

[3] Howard, THIS JOURNAL, 47, 455 (1925).

Anal. Calcd. for $C_{10}H_9O_2Br_3$: Br, 59.81 Found: Br, 59.75.

The melting point of the propionate is 70.5".

Anal. Calcd. for $C_{11}H_{11}O_2Br_3$: Br, 57.79. Found: Br, 57.85.

In the case of the butyrate the use of the anhydride did not give as satisfactory results as butyryl chloride, with which the carbinol was heated at 60–90° for three hours. Even after careful purification and distillation this ester does not solidify on standing for several weeks at room temperature. It is a thick viscous liquid of b. p. 205–207° at 220 mm., d_{20}^{20} 1.779.

Anal. Calcd. for $C_{12}H_{13}O_2Br_3$: Br, 55.90. Found: Br, 55.85.

The benzoate was prepared by treatment with benzoyl chloride according to the usual procedure of the Schotten–Baumann reaction. On recrystallization from 95% alcohol clusters of needles are obtained. It melts at 146°.

Anal. Calcd. for $C_{15}H_{11}O_2Br_3$: Br, 51.81. Found: Br, 51.76.

The average yield of all of these esters was 85%.

All of the esters are insoluble in water and with the exception of the benzoate readily soluble in carbon disulfide, ethyl alcohol, methyl alcohol, benzene, acetone, ether, chloroform and carbon tetrachloride, the benzoate being much less readily soluble in ethyl and methyl alcohols than the others.

Summary

Tribromomethylphenylcarbinol and its acetic, propionic, butyric and benzoic esters have been prepared and studied.

MISSOULA, MONTANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND THE UNIVERSITY OF TARTU (DORPAT), ESTONIA]

SYNTHESIS OF 1,4-PENTADIENE

BY PAUL N. KOGERMAN

RECEIVED OCTOBER 20, 1930 PUBLISHED DECEMBER 18, 1930

Among various series of unsaturated hydrocarbons the least explored field is that of the 1,4-dienes. According to Beilstein's "Handbook" only a few open-chain 1,4-dienes are known, *i. e.*, hexadiene-1,4, and 4-propylheptadiene-1,4. The first member of the series of diolefins with isolated double bonds has attracted the attention of many chemists. Several investigators have tried to prepare 1,4-pentadiene. Demjanov[2] and Demjanov and Dojarenko[3] on heating pentamethylenediamine nitrate or treating 1,5-di-iodopentane with alcoholic potash obtained among other products a small amount of a substance which on bromination yielded the tetrabromide of 1,4-pentadiene. Thiele[4] and others tried to prepare the hydrocarbon by exhaustive methylation of piperidine but

[1] Beilstein, "Handbuch org. Chem.," 1918, Bd. I, p. 253.

[2] Demjanov, *J. Russ. Phys.-Chem. Soc.*, 26,665 (1894).

[3] Demjanov and Dojarenko, *Ber.*, 40, 2589 1908).

[4] Thiele, *Ann.*, 319, 228 (1901).

obtained its isomer, 1,3-pentadiene. Recently Dojarenko[5] found that on catalytic dehydration of cyclopentanol a small amount of 1,4-pentadiene is formed. All these investigators failed to obtain the pure hydrocarbon. The final stage of the above-mentioned reactions favors molecular rearrangements. It seemed to the author most natural to avoid high temperatures and strong reagents, and in a manner analogous to the preparation of diallyl from allyl bromide[6] to bind vinyl and allyl radicals, using their bromides and magnesium

$$CH_2{=}CHCH_2Br + CH_2{=}CHBr \xrightarrow{Mg} CH_2{=}CHCH_2CH{=}CH_2 + MgBr_2$$

Starting from this point of view the author treated a mixture of vinyl bromide and allyl bromide with magnesium in anhydrous ether; the experiment was successful but the yield of the hydrocarbon was rather low. To increase the yield various modifications of the method were studied. First of all it was attempted to prepare vinylmagnesium bromide, and treat this Grignard compound with allyl bromide. Contrary to expectation, which was based on the researches of Austerweil[7] and Krestinsky,[8] vinyl bromide did not react with magnesium in dry ether under ordinary conditions. Then it was tried *vice versa* to treat ally magnesium bromide with vinyl bromide, using an excess of the latter. The method of Gilman and McGlumphy[9] was used for preparation of allylmagnesium bromide. The Grignard compound was heated in a pressure bottle with three times the theoretical amount of vinyl bromide: the result was negative. One is inclined to assume that allylmagnesium bromide *in statu nascendi* is more active or "activates" vinyl bromide, thus favoring the formation of vinylmagnesium bromide.

Further it was found that the size of the magnesium turnings or particles has some effect on the yield of the hydrocarbon. The best results were obtained with magnesium-copper-alloy,[10] finely ground. Increase in the rate of the reaction also increases the yield of the diolefin. The 1,4-pentadiene obtained by this anomalous Grignard reaction is not pure; after removal of ether with strong hydrochloric acid,[11] the liquid contains a fair amount of vinyl bromide, 1,4-pentadiene and 1,5-hexadiene.

The only way to recover the pure 1,4-pentadiene is via its tetrabromide. The researches of Tissier and Grignard,[12] v. Braun and Sobecki,[13] and

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[5] Dojarenko, J. *Russ. Phys.-Chem. Soc.*, 58, 29 (1926).

[6] Meisenheimer and Casper, *Ber.*, 54, 1655 (1921).

[7] Austerweil, German Patent 245,180; *Chem. Centr.*, I, 1267 (1912).

[8] Krestinsky, *Ber.*, 55, 2770 (1922).

[9] Gilman and McGlumphy, *Bull. soc. chim.*, [4] *43,1322* (1928).

[10] Gilman, Peterson and Schulze, *Rec. trav. chim.*, 47, 19 (1928).

[11] Compare Cortese, THIS JOURNAL, 51,2267 (1929).

[12] Tissier and Grignard, *Compt. rend.*, 132,835 (1901).

[13] V. Braun and Sobecki, *Ber.*, 44,1918 (1914).

others show that 1,2-dibromides react with magnesium, forming unsaturated hydrocarbons, *i. e.*, regenerating the double bond. The same method was used for regenerating 1,4-pentadiene from its tetrabromide, about 85% of the original hydrocarbon being recovered. The pure 1,4-pentadiene boils at 25.8–26.2°. The yield of the hydrocarbon is about 15% of the theoretical, based on vinyl bromide.

Experimental

Preparation of Vinyl Bromide.—The Swarts[14] method for preparation of vinyl bromide from ethylene bromide and alcoholic potash is not quite satisfactory for preparing larger quantities of vinyl bromide. Therefore the method was improved by introducing the following modifications.

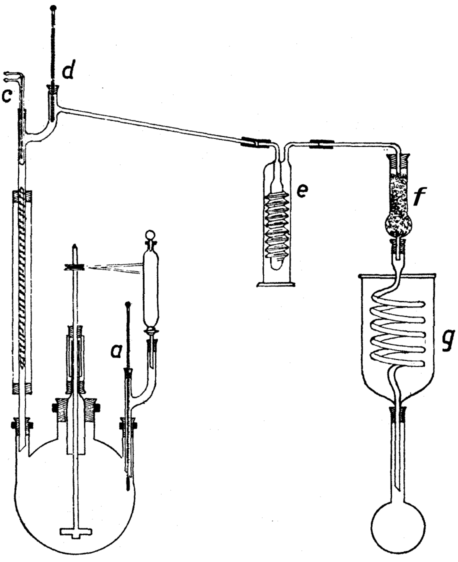

Fig. 1.—Apparatus for preparation of vinyl bromide.

A 1.5-l. flask with three necks is provided with a stirrer (through central neck), with a dropping funnel, and a dephlegmator or Vigreux column, surrounded by a jacket through which water at 17° is circulated (see Fig. 1). The column is connected (in succession) with a wash-bottle, calcium chloride tube and a Staedeler condenser (cooled by means of a freezing mixture). The receiver is also surrounded with freezing mixture. Into the flask is put an alcoholic solution of potassium hydroxide, made from 175 g. of potassium hydroxide, 350 cc. of water and 650 cc. of 96% ethyl alcohol. The solution is stirred and heated on a water-bath up to about 60°. Then 195 g. of ethylene bromide is dropped slowly into the flask. In a few minutes evolution of vinyl bromide begins. By circulating water in the jacket the speed of distillation is regulated so that the temperature of the vapor leaving the column is about 18°. The operation takes about an hour and a half. Then the solution of potassium hydroxide can be removed from the flask by a siphon, the dropping funnel charged with a fresh portion of ethylene bromide and the operation started again. The yield of vinyl bromide from 195 g. of ethylene bromide is 90–100 g. or about 85%. Vinyl bromide obtained by this method is dry and pure; b. p. 16–17°.

Allyl bromide was prepared by the method of Adams;[15] the fraction of b. p. 70–71° was used.

Preparation of 1,4-Pentadiene. (1) Under Atmospheric Pressure.—A 100-cc. round-bottomed pyrex flask is provided with a mercury-sealed stirrer, dropping funnel and Staedeler condenser, surrounded with freezing mixture; 2.65 g. of magnesium, 0.5 g. of iodine and 0.1 mole of ethylene bromide dissolved in about 40 cc. of dry ether is intro-

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[14] Swarts, *Chem. Centr.*, II, 804 (1901); *Bull. acad. Roy. Belgique,* 383 (1901).

[15] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 3.

duced into the flask; 16–17 g. of allyl bromide in about 15 cc. of ether is then slowly dropped into the flask, with stirring of the mixture. In a few minutes the reaction starts. After the reaction ceases the flask is heated for about one hour and cooled. The reaction products are then distilled, using a Widmer column, and two fractions collected: one (i) taken up to the initial decomposition point of the etherates, and (ii) up to 36°. Both fractions are cooled in a freezing mixture, then bromine is slowly added (shaking the flasks) until the color of bromine remains. After bromination the flasks are allowed to stand in a freezing mixture for about two hours. Then the ether is evaporated under reduced pressure, and the contents of the flasks dissolved in hot alcohol. On cooling, crystals (colorless leaflets) of 1,4-pentadiene tetrabromide appear. The ii fraction always contains a certain amount of the tetrabromide of 1,5-hexadiene. The crystals are filtered, dried and weighed. After recrystallization from hot ethyl alcohol, the crystals of 1,4-pentadiene tetrabromide melt at 85.8–86°.

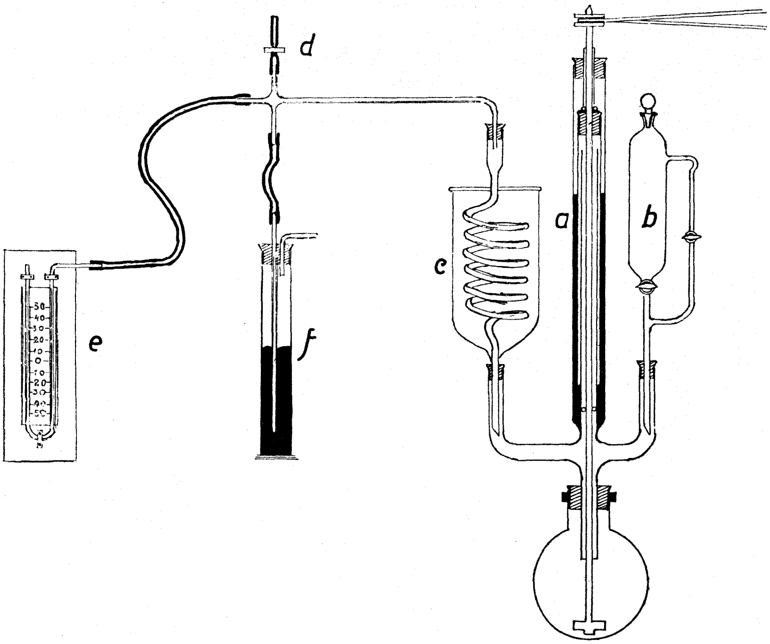

Fig. 2.—Apparatus for preparation of 1,4-pentadiene under pressure.

(2) Under **Pressure.**—When the reaction proceeds violently some vinyl bromide is carried through the condenser uncondensed. To avoid losses the reaction can be carried out in a closed system, under a pressure of 260–270 mm. For this purpose a 100-cc. round-bottomed flask is provided with a rubber stopper through which passes a tube with two side tubes; through the central tube is a mercury-sealed stirrer; the height of the mercury column is about 320 mm. (see Fig. 2a), one side tube is fitted with a dropping funnel, b, the other with Staedeler condenser, c. The body of the funnel is connected with its outlet tube below the stopcock by means of a narrow glass tube. The spiral condenser is connected with a manometer, e, and a mercury seal, f. The height of the mercury column in f is regulated so that the pressure in the apparatus does not exceed 280–290 mm.

For the production of larger quantities of the compound, a 750-cc. round-bottomed flask was used. and the dimensions of other parts of the apparatus were correspondingly larger.

Thirteen and two-tenth grams of magnesium and 0.5 g. of iodine were placed in the flask; from the dropping funnel about 100 cc. of anhydrous ether containing 1 g. of allyl bromide was added. In few minutes the reaction begins. The pinchcock clamp, d, is opened, and air is driven out by the ether vapor. Next 56 g. of vinyl bromide in 100 cc. of anhydrous ether is introduced into the flask, and then 75 g. of allyl bromide in 70 cc. of ether is slowly added in the course of about eighty to ninety minutes. During the reaction the manometer shows about 240–260 mm. pressure; when the pressure rises above that indicated, the flask must be cooled. After the whole portion of allyl bromide has been added the reaction mixture is heated on a water-bath until the pressure begins to fall. The reaction products are distilled, and the distillate is brominated. The yield of crude tetrabromide is about 45 g. or 22% of the theoretical from the vinyl bromide. After recrystallization from hot alcohol, about 25–28 g. of tetrabromide, m. p. 85–86', is obtained.

Anal. Calcd. for $C_5H_8Br_4$: C, 15.47; H, 2.08; Br, 82.47; mol. wt., 387. Found: C, 15.53; H, 1.99; Br, 82.52; mol. wt., 376.

The yield of crystals under various conditions of the experiment is given in Table I.

TABLE I

Expt.	Mg, g.	CH_2= CHBr, g.	CH_2= CH— CH_2Br, g.	CHI— $CHCH_2Br$, time of addition, min.	Bromine, cc.	Tetrabromide (crude), g.	Crystals, m. p. 85–86° g.	Remarks
1	2.65	10.8	16.2	18	0.8	1.9	1.2	Mg Schering Kahlbaum
2	2.65	12.7	18.3	110	.9	..	1.75	Mg Schering Kahlbaum
3	2.65	10.8	16.0	16	1.7	..	3.8	Ground Mg
4	2.65	12.7	17.4	120	2.2	6.7	4.0	Ground Mg
5	2.65	10.6	15.3	30	3.3	10.2	6.6	Finely ground Mg under pressure
6	2.65	10.8	15.9	75	2.4	7.1	4.5	Finely ground Mg under pressure
7	2.65	10.55	12.3	30	21	5.9	3.8	Finely ground Mg under pressure

Tetrabromides of **1,4-Pentadiene.**—When the mother liquor from recrystallization of the solid tetrabromide is diluted with water, an oily liquid is precipitated. As theoretically two isomeric tetrabromides are possible, an attempt was made to isolate the other isomer. About 160 g. of washed and dried heavy liquid was distilled under reduced pressure using a Widmer column as still-head. From the distillate, on cooling, about 60 g. of crystalline pentadiene tetrabromide (m. p. 85–86°) and about 55 *g.* of diallyl tetrabromide were obtained; about 45 g. of the distillate remained liquid. After repeated fractionation crystals again separated from the distillates. Finally, about 10 g. of oily bromide, boiling from 115–123° (1–2 mm.) remained. The figures obtained on the analysis of the liquid did not closely correspond to the composition of pentadiene tetrabromide but were close to the diallyl tetrabromide. Anyhow, the supposed liquid tetrabromide is formed in comparatively small quantities or it might isomerize on distillation.

Regeneration of **1,4-Pentadiene** from *its* Tetrabromide.—Regeneration of the diene was carried out in a flask provided with a stirrer, a dropping funnel and a Staedeler condenser. The condenser jacket was filled with freezing mixture. Between the flask and condenser is placed a T-piece for pushing in the dry tetrabromide (see Fig. 3).

The tetrabromide is put into the side tube, provided with a glass rod. By pushing forward the glass rod the solid tetrabromide is introduced into the condenser tube, wherefrom the ether vapor sweeps it down. This device allows the use of smaller quantities of ether because the solubility of the tetrabromide in ether is rather low, *i. e.*, about 13 g. in 100 cc. In the flask are placed 12.5 g. of magnesium, 0.5 g. of iodine and 3 g. of tetrabromide; then 35 cc. of dry ether is added. The reaction begins immediately and 33 g. of tetrabromide in 250 cc. of dry ether is then slowly added. After the dissolved tetrabromide has been added, 31 *g.* of tetrabromide is gradually pushed in through the T-piece. The reaction takes about two hours, after which the flask is warmed on a water-bath for about thirty minutes. From the reaction mixture the pentadiene and ether are distilled off. The distillate is placed in a separatory funnel, an equal amount of cooled concd. hydrochloric acid is added, and the contents of the funnel are shaken while cooling under the tap. The mixture is allowed to settle, the acid layer is drawn off and the operation is repeated. The ether-free pentadiene is successively washed with water, sodium bicarbonate solution, and again with water, then the liquid diene is dried over calcium chloride. The yield of the products from 145 g. of tetrabromide is 18.5 *g* of 1,4-pentadiene, or about 73% of the theoretical.

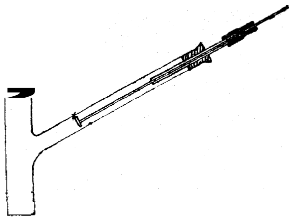

Fig. 3.—T-piece for pushing in solid pentadienetetrabromide.

The total amount of 1,4-pentadiene recovered, as determined by bromination of the distillate is about 85%.

The hydrocarbon was fractionated using a Widmer column as stillhead. A few drops of liquid passed over below 25° and about 70% of the liquid at 25.8–26.2°. The whole boiled below 26.6°. The liquid has a weak characteristic odor.

Properties of **1,4-Pentadiene.**—B. p. 25.8–26.2° at 756 mm.; d_4^{20} 0.6594; n_D^{20} 1.3883; mol. refraction: calcd., 24.26; found, 24.26; mol. wt. (Victor Meyer method): calcd. 68.08; found, 68.66

In conclusion, the author desires to record his thanks to Professor E. P. Kohler for his interest in the work, and to Mr. H. Raudsepp for checking the experiments.

Summary

1. An improved method for preparation of vinyl bromide has been worked out.

2. Two modifications of a new method for the synthesis of 1,4-pentadiene are described.

3. For the first time 1,4-pentadiene has been prepared in pure condition and its properties determined.

4. The bromination products of 1,4-pentadiene were investigated

TARTU (DORPAT), ESTONIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 67]

THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. XI. THE INFLUENCE OF THE STRUCTURE OF THE SUBSTITUENT ON THE TEMPERATURE OF DECOMPOSITION OF CERTAIN DERIVATIVES OF MALONIC ACID

BY JAMES F. NORRIS AND RALPH C. YOUNG

RECEIVED OCTOBER 21, 1930 PUBLISHED DECEMBER 18, 1930

For a number of years a major problem in this Laboratory has been the study of the influence of the structure of substituents on the lability of the atomic linkings in certain organic compounds. In the earlier work[1] the rates were determined at which such linkings were severed when analogous compounds reacted with a fixed reagent under the same conditions. An interpretation of these results led to conclusions in regard to the effect of the structure of a radical on the lability of certain bonds. In the last communication on this subject[2] a second method of comparing the relative lability of bonds was described. The temperatures at which the C—O bond was broken by heat alone in compounds of the type $(C_6H_5)_3C$-OR were determined. It was shown that these temperatures could be determined in separate experiments within ±2° when the substances were heated under fixed conditions. A comparison of the averages of the values obtained in this way in the case of ten ethers with those obtained from the study of the same bond by means of reaction velocities brought out the striking fact that the two methods gave comparable results. There appears, therefore, to be a relation between the temperature at which a bond is broken by heat and the rate at which it is broken when a chemical reaction involving this bond takes place.

This conclusion appeared to be sufficiently important to warrant further investigation. Malonic acid and its derivatives of the type $RHC(COOH)_2$ decompose smoothly when heated into RH_2CCOOH and CO_2. Several such derivatives were made and the temperatures at which the decomposition began were determined. In the case of these compounds a C—C bond is broken. In the case of the esters previously studied a C—O bond was severed. It was of interest to discover if there was any relationship between the influence of the change in the alkyl radical, R, on the temperatures of pyrolysis in the two series.

In Table I are given the temperatures of decomposition of the derivatives of malonic acid and for comparison the temperatures of decompo-

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[1] (a) Norris and others, THIS JOURNAL, 47, 837 (1925); (b) 49, 2640 (1927); (c) 50, 1795 (1928); (d) 50, 1804 (1928); (e) 50, 1808 (1928); (f) 50, 1813 (1928); (g) 50, 3042 (1928).

[2] Norris and Young, *ibid.*, 52, 753 (1930).

TABLE I

EXPERIMENTAL DATA

Radical	Temp. (°C.) of decomposition $RHC(COOH)_2$	Difference in decomp. temp.	Temp. (°C.) of decomposition $RO—C(C_6H_5)_3$	Difference in decomp. temp.	Vel. constants RO—H with p-$NO_2C_6H_4COCl$
None	128				
Methyl	120	8	262		0.184
		10		20	
Ethyl	110		242		.85
		11		12	
n-Propyl	99		230		.066
		9		9	
n-Butyl	108		239		.074
		18		19	
Isopropyl	90		220		.010

sition of the triphenylmethyl ethers containing the same alkyl radicals. There is also included the velocity constants of the reactions between *p*-nitrobenzoyl chloride and the alcohols containing these radicals.

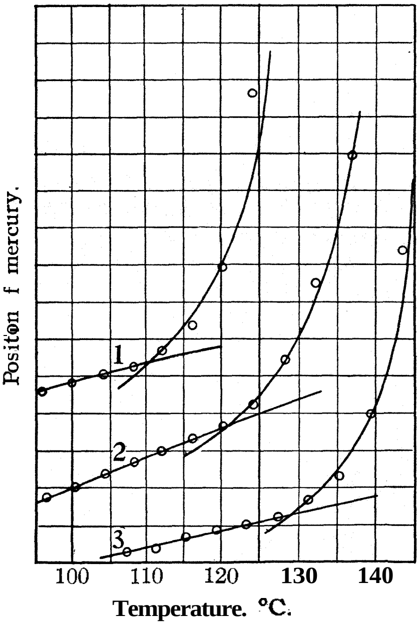

Fig. 1.—Position of mercury above an arbitrary zero for various values of the temperature. Each division = 10 cm. displacement: 1, ethylmalonic acid; 2, methylmalonic acid; 3, malonic acid.

It will be seen from the figures in the table that the temperatures at which decomposition takes place decrease as the radical is changed from methyl to ethyl and to n-propyl, but increase when n-propyl is replaced by n-butyl. This holds true in both series of compounds.

It is also a striking fact that the actual changes of the decomposition temperatures are the same in the two series, within the limits of accuracy of measurement, except in the case of the replacement of the methyl radical by ethyl.

In the two series the temperatures of decomposition fall in the same order as the velocity constants of the reactions between *p*-nitrobenzoyl chloride and the alcohols containing the same alkyl radicals present in the acids and ethers.

The position of the changing substituent relative to the bond severed is the same in the two series of compounds. In both cases the substituent is in combination with an element

(C or O) a second bond of which is severed by heat. This is made clear by writing the formulas of the two classes of compounds as follows, and indicating the bonds which are severed in pyrolysis

$\overset{\text{H}}{\underset{\text{COOH}}{\text{RC}}}\text{—COOH}$ and $\text{RO—C}(C_6H_5)_3$

The interpretation of the results leads to a reasonable conclusion. The change in the nature of R affects the strength of the linking between the radical and the carbon atom in one series and the oxygen atom in the other. These changes affect, in turn, the strength of the bond between these elements and the groups which are removed *as* the result of pyrolysis. The results furnish, thus, experimental evidence of the interrelationship between the affinities of an atom. It was an unexpected fact that the effects on the strength of the bonds of the carbon atom and of the oxygen atom were approximately the same with the same change in radical when measured by the change in temperature necessary to bring about the rupture of the bonds of the two elements.

Other cases of the effect of varying substituents on the temperature at which definite bonds are broken by heat are now being studied to discover if the simple relationships here emphasized are general. Work on certain aliphatic hydrocarbons is well advanced.

Experimental Details

Preparation of the Acids Used.—The derivatives of malonic acid were prepared in the usual way from ethyl malonate. The acids were crystallized from benzene several times until the behavior was constant when melting points were determined.

Method of Determining Decomposition Temperatures.—The method used was similar to that described in the paper on the pyrolysis of certain triphenylmethyl-alkyl ethers.[2] It consisted, in brief, in heating the material in a closed glass tube connected with a horizontal capillary tube containing a drop of mercury, and recording from time to time the position of the mercury on a scale as the temperature was raised at a definite rate. At the decomposition point there was a marked increase in the rate in the change of position of the mercury. One-half gram of malonic acid and equivalent amounts of the other acid were used in the experiments. The temperature of the bath was allowed to rise one degree in approximately forty-five seconds. The observations were plotted and curves drawn through the points recorded.

The accompanying plot indicates the nature of the curves obtained with three of the acids studied. The values of the decomposition temperatures recorded were obtained by plotting all the results accurately on a large scale.

The procedure described above was checked, in the case of malonic acid, by a chemical method. The acid was heated in a tube connected with another containing a solution of barium hydroxide. Air free from carbon dioxide was drawn rapidly through the two tubes, and the acid and the solution were then introduced. The stream of air was continued, and the tube containing the acid was heated at such a rate that the temperature rose about one degree per minute. The temperature observed when the first opalescence appeared in the barium hydroxide was taken as the decomposition temperature. The results obtained in this way in separate experiments agreed with those obtained by the physical method to within ± 1°.

In Table II are given the melting points and decomposition temperatures of the acids as observed by the authors and the previously published values recorded in Beilstein's "Handbuch," The two sets of numbers in the column headed "Temperature of Decomposition Observed by Authors" are the results of independent experiments.

TABLE II

MELTING POINTS AND DECOMPOSITION TEMPERATURES OF DERIVATIVES OF MALONIC ACID

Acid	Melting points (°C.) observed by authors	Melting points (°C.) recorded in Beilstein	Decomp. temp. (°C.) observed by authors		Decomp. temp. (°C.) recorded in Beilstein
Malonic	129–131	130.5 to 135.6	127	129	140-150
Methylmalonic	120–122	125 to 135	120	120	120
Ethylmalonic	110–111.5	111.5	110	110	160
***n*-Propylmalonic**	94–96	96.0	100	98	150
n-Butylmalonic	99.5–101.5	101.5	108	108	150
Isopropylmalonic	85–87	87.0	90	90	120

The melting points were determined in the usual way in capillary tubes. The lack of sharpness in these values was no doubt due to the fact that they lie so close to the temperatures at which decomposition takes place.

The decomposition temperatures recorded in Beilstein's "Handbuch" were determined by observing the behavior of the acids when heated in melting-point tubes. There is no claim for exactness.

Summary

1. The temperatures have been determined at which malonic acid and certain of its alkyl derivatives break down into carbon dioxide and monobasic acids.

2. The influence of the radicals studied on the decomposition temperatures is of the same order of magnitude as that found in the earlier study of the pyrolysis of triphenylmethyl-alkyl ethers; the temperature is lowered in the two series as the radical is changed from methyl to ethyl to *n*-propyl but rises when n-butyl is present. The isopropyl radical derivatives in the two series decompose at lower temperatures than the n-propyl compounds.

3. In both series of compounds the decomposition temperatures fall in the same order, with varying alkyl radicals, as the rates at which alcohols containing the same radicals react with an acyl chloride. There appears to be a relationship between the effect of a radical on the lability of a bond as measured by the temperature of pyrolysis and the rate at which the bond is broken in a chemical reaction.

CAMBRIDGE, MASSACHUSETTS

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

OPTICALLY ACTIVE DIAZO COMPOUNDS. DIAZOCAMPHANE

BY ULRICH HEUBAUM AND WILLIAM ALBERT NOYES

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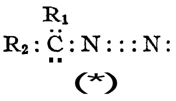
The question whether or not a carbon atom which is attached to a diazo group might cause optical activity has been the subject of a great number of investigations during the last ten years.

On the one hand the results of the investigations of Levene and Mileska[1] in 1921 and of Noyes and Chiles[2] in 1922 imply an asymmetry of a carbon atom which is bound to diazo nitrogen. These investigators prepared the diethyl-a-diazo-succinate in which the only possible asymmetric carbon atom is connected to a diazo group and they found the compound to possess a small optical rotatory power. This fact has recently been confirmed by H. Lindemann[3] and his co-workers. The straight-chain formula established by Angeli and Thiele[4] and modified by Noyes[5] according to the octet theory explains the asymmetry of the carbon atom (A). In this formula the carbon atom represents a center of asymmetry since it is bound to three different substituents and possesses one electric charge.



$R_2:\overset{R_1}{\underset{\cdot\cdot}{\ddot{C}}}:N:::N:$

On the other hand, some qualities of the diazo compounds seem to justify the ring structure rather than the open-chain formula.[6]

This work has been undertaken in order to get further evidence of the behavior of alicyclic diazo compounds. Diazocamphane (B) contains, besides the carbon atom which is connected with the diazo group, the two asymmetric carbon atoms of the camphor. It, therefore, can be expected to exist in four optically active modifications which give two pairs of optical antipodes and two pairs of stereoisomers. The d-camphor consequently furnishes two stereoisomeric diazo compounds and in the same way two stereoisomeric amines or chlorides.[7]

The diazocamphane $C_9H_{16}=C=N_2$ has been prepared in ethereal solu-

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[1] Levene and Mileska, J. *Biol. Chem.*, 45,592 (1921); 52,485 (1922).

[2] Chiles with Noyes, THIS JOURNAL, 44, 1798 (1922).

[3] H. Lindemann, Wolter and Groger, *Ber.*, 63,702 (1930).

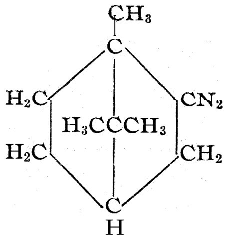
[4] A. Angeli, *Atti accad. Lincei*, [V] 32, i, 443 (1923). J. Thiele, *Ber.*, **44**, 2522 (1911).

[5] Kendall with Noyes, THIS JOURNAL, 48, 2404 (1926). Staudinger [*Helv. Chim. Acta*, **5**, 75 (1922)], by a study of the addition of phosphines to diazo compounds, also found the open-chain formula to be more probable.

[6] See, for instance, Sidgwick, J. *Chem. Soc.*, 1108 (1929), and Lindemann and Thiele, *Ber.*, 61, 1529 (1928).

[7] Only one of the bornyl chlorides derived from the d-camphor, the dextrorotatory bornyl chloride, has been known until now. Studying the reaction of the diazocamphanes with hydrochloric acid, we have prepared very small amounts of the corresponding stereoisomeric levorotatory form.

tion from the normal and the neo-bornylamines, both of which are formed by the reduction of d-camphor-oxime and represent stereoisomers. The ethereal solution of both of the diazocamphanes is deeply red colored and extremely unstable. Even below 0° the compounds decompose with the evolution of nitrogen and the formation of the inactive polycyclic hydrocarbon tricycene. This reaction proves the old assumption that the diazocamphane is temporarily formed as an intermediate product in the preparation of tricyclene by the oxidation of camphor-hydrazone with mercuric oxide.[8]

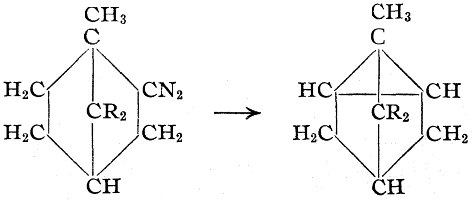


(B)

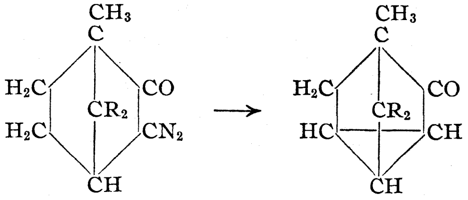
$$C_9H_{16}:C:NNH_2 + HgO \longrightarrow C_9H_{16}:C:N_2 \longrightarrow C_{10}H_{16} + N_2$$

Furthermore, the diazocamphane is very sensitive to hydrogen ions. Even carbon dioxide favors its decomposition.

Tricyclene was found to be the only product of the spontaneous decomposition of the diazocamphane. No nitrogen-containing compounds such as ketazides or bis-hydrazones have been observed. This decomposition is analogous to that of the diazocamphor



Diazocamphane → Tricyclene (α-pericyclocamphane)



Diazocamphor → β-Pericyclocamphanone

When cooled to a temperature of a carbon dioxide–acetone mixture, the compound could be kept without appreciable decomposition for several days.

Attempts to crystallize the diazocamphane from its solution failed because of its instability.

The specific rotations of both of the diazocamphanes are very high, ranging between about +60 and +450°.

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[8] Friedlander, "Fortschritte der Teerfarbenfabrikation," German Patent 353,933 (1922). Because of the instability of the diazocamphane it is impossible to prepare it by this reaction. Staudinger, Ber., 53,1106 (1920).

For determining the concentration of the diazo solutions, the gasometric method was used. The diazo compound was decomposed by dilute sulfuric acid and the volume of nitrogen evolved was measured. In some cases the two diazo compounds have been compared colorimetrically. The readings of the rotation were taken at about −5°, at which temperature the compound decomposes very slowly. On account of the relatively great inaccuracy of this method in connection with the instability of the diazo compound, the values for the specific rotation vary considerably. The average values of the specific rotation of the diazocamphanes for light of different wave lengths are given in Table I.

Table I

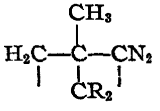
Specific Rotation of Normal Diazocamphane

λ	615	603	592	584	572
$[\alpha]$	179	164	196	350	420
λ	568	557	547	538	530
$[\alpha]$	411	411	339	286	71

Specific Rotation of Neo-diazocamphane

λ	645	635	602	592	585
$[\alpha]$	170	238	279	275	320
λ	578	572	567	558	
$[\alpha]$	455	466	420	398	

The dispersion curve of each of the diazo compounds shows its highest value in the light green part of the spectrum, beginning with a λ of about 5750 Å., and then goes down very rapidly in yellow and blue light. The anomaly of the dispersion curve in this part of the spectrum is caused by an absorption band which is located at about λ5650 Å. (Cotton effect)[9] (Fig. 1) This absorption band is undoubtedly due to the diazo group. It possesses a strong vicinal effect upon the substituents of the one asymmetric carbon atom of the original camphor (C), thus increasing its asymmetry and causing the extremely high rotation.[10] Similar effects have been observed with other alicyclic diazo compounds, e. g., the methyl γ-diazocamphonanate of Noyes and Kendall.[5]



$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ H_2C & — & C & — & CN_2 \\ | & & | & & | \\ & & CR_2 & & \end{array}$$

(C)

While the study of the single values of the specific rotation did not seem to give satisfactory evidence concerning a difference of the two diazo compounds, a consideration of the whole dispersion curves seemed to be more successful. The curve obtained from the normal compound rises very rapidly toward the green and then shows a rather slow inflection near the maximum. The curve from the neo-compound rises very rapidly, too, but then shows a very strong inflection near the maximum (Fig. 1).

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[9] Cotton, Ann. *chim. phys.*, [7] 8,347 (1896).

[10] W, Kuhn, Ber.. 63,200 (1930).

The curves plotted from the original observations, as shown in Fig. 2, bring out the differences between the two compounds more clearly. In these curves the inaccuracies of the volumetric determinations of the quantities present are eliminated. Two different solutions were used for each compound. It will be seen that the shapes of the two curves for the normal compound are alike and are different from the shapes of the two curves for the neo compound.

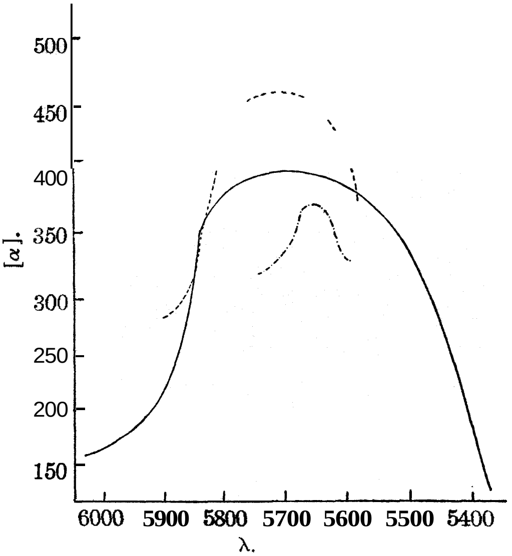


Fig. 1.—Rotatory dispersion of normal and neo-diazocamphane: ———, normal diazocamphane; - - -·- -, neo-diazocamphane; —·—·—·—, absorption curve.

Another evidence showing a difference of the two diazocamphanes was obtained in studying their decomposition products. A rather concentrated ethereal solution of diazocamphane decomposes with ethereal hydrochloric acid forming tricyclene and small amounts of bornyl chloride. The bornyl chloride obtained from the normal diazocamphane was levorotatory, having a specific rotation of $[\alpha]_D$ $-33.2°$ in ether. It thus represents the stereoisomer of the ordinary

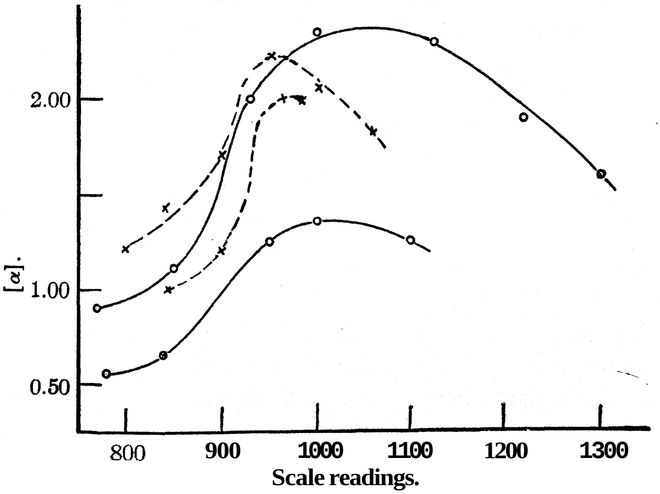
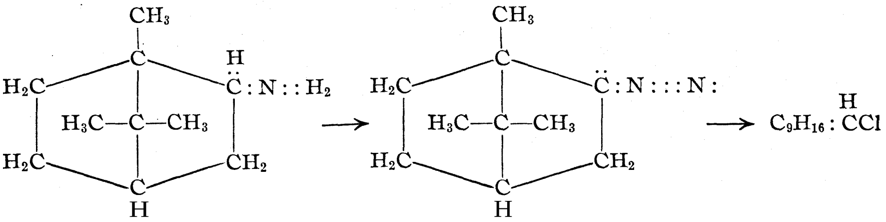


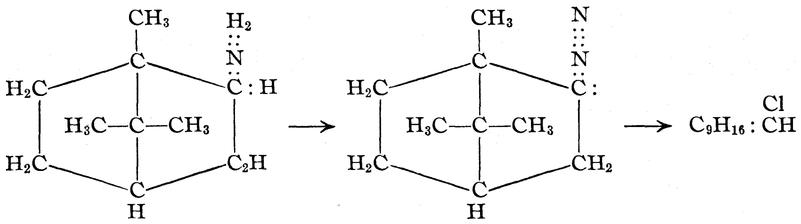
Fig. 2.—Observed rotations of normal and neo-diazocamphane: ———, normal; — — — —, neo.

dextrorotatory bornyl chloride. The neo-diazocamphane decomposed under the same conditions with the formation of a very small amount of bornyl chloride, the specific rotation of which we have been unable to determine but it was found to be dextrorotatory.

The fact that the two diazo compounds give different decomposition products and that their dispersion curves have different shapes indicates that their structure must be different. Their behavior might be explained by the following diagrams.

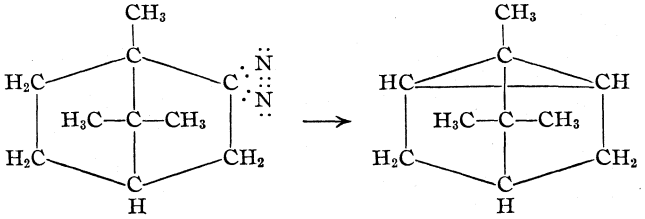


Normal bornylamine ⟶ Normal diazocamphane ⟶ Normal bornyl chloride



Neo-bornylamine ⟶ Neo-diazocamphane ⟶ Neo-bornyl chloride

On the other hand, the formation of tricyclene from both diazo compounds indicates that they may have the same structure, in part. This can be explained by the cyclo form



Cyclo-diazocamphane Tricyclene

The loss of a molecule of nitrogen from this cyclo form would leave a bivalent carbon atom bearing two electrons. This would be followed by the transfer of a hydrogen ion from the CH_2 group to these two electrons and the formation of the bridge across the ring.

The fact that mainly tricyclene and only very little bornyl chloride is formed in each case indicates that the diazocamphane consists mostly of the cyclic form, which is in equilibrium with the chain form.

This idea has recently been suggested by Lindemann,[3] while Sidgwick[6] has advocated the cyclic formula. Further evidence for the existence of optically active chain forms has very recently been secured by Ray[11] through his study of the decomposition of the two methyldiazocamphonanates obtained from the methyl esters of the cis and *trans* aminocamphonanic acids.

Experimental Part

Normal bornylamine, $C_{10}H_{17}NH_2$ and neo-bornylamine are formed by the reduction of camphor-oxime with sodium and amyl alcohol.[12] Normal bornylamine is formed chiefly and was separated from the mixture by fractional crystallization of the chlorides from water. The hydrochloride of the normal amine is much less soluble in water than that of the neo-base. The rotation of 1.36 g. of normal bornylamine hydrochloride in 100 cc. of absolute alcohol was $[\alpha]_D$ +22.6°. The melting point of the free amine was found to be 162.5–163° and its rotation in absolute alcohol $[\alpha]_D$ +45.9°. These values are in close agreement with those obtained by Forster.

Since the bornylamine, being a very strong base, forms a stable nitrite with nitrous acid it is impossible to obtain the diazocamphane by treating the primary amine with N_2O_3. We therefore used the method indicated by v. Pechmann,[13] that of treating the nitroso derivative of an acyl amine with alkali.

N,N′-Dibornylurea, $(C_{10}H_{17}NH)_2CO$, has been obtained by treating an ethereal solution of normal bornylamine cooled to −15° with an equivalent amount of phosgene dissolved in toluene. After evaporating the ether and toluene the residue was purified by recrystallization from aqueous alcohol.[14] The urea sublimes in long needles without melting. In this method the theoretical yield is only 50% since one-half of the amine is converted into the hydrochloride. It can easily be prepared, however, when using diphenylcarbonate, giving a yield of practically 100%.[15]

Mononitroso normal bornylurea has been prepared by passing carefully dried N_2O_3 into the ethereal solution of the urea cooled to −15° until it is colored green and keeping the solution at this temperature for about two hours. The solution is washed first with water and then twice with an ice cold solution of sodium bicarbonate. It is dried by freezing out the water at −80° and filtering off the ice. After evaporating the ether the nitroso compound crystallizes in yellow needles which are quite stable at 0° when kept over phosphorus pentoxide. The compound gives a positive Liebermann test for the nitroso group.

Anal. Subs., 0.3205: N_2, 31.6 cc. (24°, 752 mm.). Calcd. for $C_{10}H_{17}NH{-}CO{\cdot}(NO)NC_{10}H_{17}$: N, 11.63. Found: N, 11.5.

The crystals melt between 73 and 75° with decomposition. The nitroso compound is readily soluble in ether and alcohol. It slowly decomposes at room temperature, changing back into the urea. With sodium hydroxide or sodium methylate the yellow ether solution turns red, forming the diazo compound according to the equation

$$C_{10}H_{17}N(NO)CONHC_{10}H_{17} \xrightarrow{KOH} C_9H_{16}{=}C{=}N_2 + CO_2 + C_{10}H_{17}NH_2$$

This equation shows that only 50% of the amine applied can be converted into the diazo

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[11] F. E. Ray, THIS JOURNAL, 52,3004 (1930).

[12] Forster, J. *Chem. Soc.*, *73*, 386 (1889).

[13] Von Pechmann, *Ber.*, 27, 1888 (1894).

[14] Neville and Pickard, J. *Chem. Soc.*, 65,687 (1894).

[15] Heubaum, THIS JOURNAL, 52,2149 (1930).

compound, which means a considerable loss of the raw material. Furthermore, the diazo solution is contaminated by bornylamine, which can hardly be separated. We therefore found the urethane derivative of the bornylamine more useful for the preparation of the diazo compound since all of the amine is turned into the diazo compound. The diazo solution obtained in this way does not contain any contaminating by-products

$$C_{10}H_{17}N(NO)COOC_2H_5 \xrightarrow{\text{KOH}} C_9H_{16}{=}C{=}N_2 + CO_2 + C_2H_5OH$$

Normal bornyl urethane has been obtained by the action of an excess of chloroethyl carbonate on normal bornylamine, which was suspended in aqueous potassium hydroxide at 0°. The product was then extracted with ether and purified by recrystallization from aqueous alcohol. All of the amine was thus converted into the urethane. The urethane melted sharply at 93° (Neville and Pickard found 89°)[14] and gave a specific rotation of $[\alpha]_D$ −10.9° in absolute alcohol and $[\alpha]_D$ +3.1° in absolute ether (Neville and Pickard found $[\alpha]_D$ +6.43 in chloroform). The urethane has also most easily been prepared by warming equivalent amounts of the amine and phenylethyl carbonate on the water-bath, only the phenoxy radical being substituted by the amine.[15]

Nitroso normal bornylurethane was obtained in the same way as the nitroso urea. The yellow crystals are more unstable at room temperature than those of the corresponding nitroso urea, turning back into the urethane (m. p. 93"). The compound gives a positive Liebermann test and a specific rotation of $[\alpha]_D$ +11° in ethereal solution. It is very sensitive to hydrogen ions and that is probably why Forster[16] failed to obtain it.

Normal **Diazocamphane.**—The dry solution of the nitroso urethane in ether was cooled to −20° and then a 2% solution of sodium methylate in methyl alcohol was added. The yellow color of the solution slowly changed to red. After standing for thirty minutes at −20° the diazo solution was washed with water to remove the sodium hydroxide and the methyl alcohol and then dried by cooling to −80°. No nitrogen evolution was observed at that temperature. The solution was analyzed by passing a measured volume (5–10 cc.) into a flask which contained dilute sulfuric acid and ether at exactly 0° and which was connected with a eudiometer. The volume of nitrogen evolved was corrected for temperature and the vapor pressures of ether and water; 6.1 cc. of diazo solution gave 7.1 cc. of nitrogen at 23" and 747 mm. This corresponds to a concentration of 0.56%. This solution had a rotation of +2.0° for λ5840 Å. which gives a specific rotation of $[\alpha]_{5840}$ +350°. A Schmidt and Haensch Universal Polarimeter was used and a 1000-watt lamp as a source of light. The light was sent through a spectroscope to obtain light of the wave length desired. On account of the high absorption, especially of the green light, by the diazo compound, exact readings were very difficult to obtain in this part of the spectrum.

Neo-bornylamine.—The separation of the pure neo-bornylamine from the mixture of the two amines was rather difficult and has been carried out in two different ways. One method indicated by Forster[17] consists in converting the amines into the oxamides and recrystallization from ethyl acetate, petroleum ether and absolute alcohol, the neo-bornyl oxamide being much less soluble in those solvents. We obtained a small quantity of the neo-bornyl oxamide in this way. The melting point was 184° and $[\alpha]_D$ −60.1°, both values in close agreement with those obtained by Forster. This method of separation, however, can only be applied to mixtures which contain 60% or more of the neo-amine. Attempts to deal with mixtures containing equal amounts of the two isomers led to the isolation of a compound which melts at 100° (the "normal-oxamide" melts at 140°) and gives a mixture of the two amines on saponification. This compound has

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[16] Forster, J. *Chem. Soc.*, 85, 1193 (1904).

[17] Forster, *ibid.*, 77, 1152 (1900).

already been described by Forster. The analysis points to the empirical formula of the bornyloxamide. It represents very probably the neo-bornyl-normal-bornyl-oxamide.

Attempts to prepare the diazo compound directly from the oxamide failed since it was impossible to obtain a nitroso derivative of the oxamide.

Since this method of separation is not very satisfactory, we carried out more successfully the method indicated by Pope and Read,[18] using d-oxymethylene-camphor. The d-oxymethylene-camphor was prepared by the method described by Bishop, Claisen and Sinclair[19] and then treated with the corresponding quantity of the mixture of the amines which were dissolved in 50% acetic acid. The normal-bornylamine-oxymethylene-camphor is almost insoluble in petroleum ether and acetone, and remains after extracting the mixture with either one of these solvents. It can be purified by crystallization from alcohol and then gives a specific rotation of $[\alpha]_D$ +380° (Pope and Read found +330°). As much as possible of the normal compound was separated in this way from the mixture. The mother liquors then contained the almost pure neo-compound. After evaporating the mother liquors, the residue was dissolved in alcohol and decomposed with bromine, bornylamine hydrochloride and bromo-oxymethylene-camphor being formed For further purification the amine then was converted into the oxamide.

Neo-bornylurethane.—The pure neo-bornyloxamide thus obtained was saponified with alcoholic potash and the amine converted into the urethane, using chloro-ethyl-carbonate. The neo-bornylurethane melted at 37° and gave a specific rotation of $[\alpha]_D$ −28.0" in absolute alcohol and of $[\alpha]_D$ −31.2" in absolute ether (Neville and Pickard found m. p. 36° and $[\alpha]_D$ −9.6° in benzene).

Nitroso neo-bornylurethane was obtained in the same way as the corresponding normal nitroso compound. Its specific rotation was $[\alpha]_D$ −18.5° in ethereal solution. In other respects it shows the same properties as the normal nitroso compound.

Comparison of Normal and Neo-diazocamphanes.—A solution of neo-diazocamphane in ether which had been obtained in the same way as the normal diazocamphane was compared colorimetrically with a normal diazo solution which had a concentration of 0.34%. The tubes of the colorimeter were cooled with carbon dioxide and acetone. According to the readings the concentration of the normal solution was to the concentration of the neo solution as 21 to 27. The neo solution, therefore, contained 0.44% of diazocamphane, and had a rotation of **a** +2.03°, which for λ5720 Å. gives a specific rotation $[\alpha]_{5720}$ +466°, while the normal solution gave a specific rotation of $[\alpha]_{5720}$ +420° in light of the same wave length.

Exact readings of the rotation in the green and blue light were rather difficult to obtain because of the high absorption in this part of the spectrum. The dispersion curves for the specific rotation of the normal diazo compound as obtained in two different samples show rather high discrepancies, because of the inaccuracy of the gasometric method.

The measurements of the absorption could be carried out only rather roughly since it was impossible to obtain accurate values because of the instability of the compound. At about λ5650 Å., however, an absorption band has been found.

The decomposition of the diazo compounds with ethereal hydrochloric acid has been carried out at −25° and the bornyl chloride separated from the tricyclene by fractional distillation *in vacuo;* 0.2192 g. of the bornyl chloride obtained from the normal diazocamphane dissolved in 5 cc. of absolute ether gave a rotation of **a** −4.2". $[\alpha]_D$, therefore, is −33.2". The amount of the dextrorotatory bornyl chloride prepared

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[18] Pope and Read, J. Chem. *Soc.*, 103,455 (1913).

[19] Bishop, Claisen and Sinclair, *Ann.*, 281,328 (1894).

from the neo-diazocamphane was so small that it was impossible to determine its specific rotation.

Summary

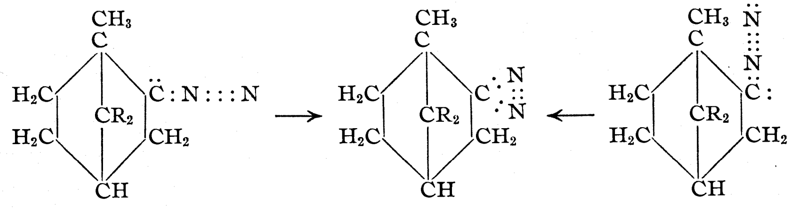
1. Diazocamphane has been prepared in ethereal solution from the nitroso urethanes of two stereoisomeric bornylamines with sodium methylate at −20°.

2. Its specific rotation varies between +60 and +450 in different parts of the spectrum.

3. The anomaly of the rotation in the green light is due to an absorption band located at about 5650 Å., caused by the $=CN_2$ group.

4. The shapes of the dispersion curves of the diazo camphanes prepared from the normal- and neo-bornylamine are different, thus indicating a difference in structure of the diazo compounds concerned.

5. Studying the decomposition of the diazocamphanes with hydrochloric acid, a new levorotatory bornyl chloride of $[\alpha]_D$ −33.2° has been prepared from the normal diazocamphane. The neo-diazocamphane gave small amounts of a dextrorotatory bornyl chloride. Both diazo compounds, however, give mainly the same decomposition product, namely, the inactive polycyclic hydrocarbon tricyclene,' which indicates that they have partly the same structure. Their behavior is explained by the following formulas



Urbana, Illinois

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

THE THERMODYNAMIC PROPERTIES OF WEAK ACIDS AND BASES IN SALT SOLUTIONS, AND AN EXACT METHOD OF DETERMINING THEIR DISSOCIATION CONSTANTS[1]

BY HERBERT S. HARNED AND BENTON B. OWEN

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Recently, Harned and Robinson[2] showed that it is possible to determine the hydrogen-ion concentration and activity coefficient of acetic acid in chloride solutions of various kinds and strengths from measurements of the electromotive forces of cells without liquid junctions. To make their calculations, the dissociation constant of acetic acid determined by conductance measurements was employed. In the present study it will be shown that an exact evaluation of the dissociation constant may be obtained from the cell measurements alone. To demonstrate the method, we shall first employ Harned and Robinson's data relating to acetic acid in sodium chloride solutions, and then present some more accurate results on formic acid in sodium chloride solutions. Finally, we shall apply the method to some weak bases by computing the dissociation constants of ammonia and some methylamines from Harned and Robinson's data. These latter will not be so exact as in the case of the acids because of an approximation introduced into the calculation, and because of the special kind of liquid junction used in the cells containing the weak hydroxides.

Since the dissociation constant of a weak electrolyte has usually been determined by the conductance method, or by electrometric methods which involve liquid junction potentials, it is a matter of considerable importance to devise a method which rests entirely upon an exact thermodynamic basis.

Outline of the Method.—Let E represent the electromotive forces of the cells

$$H_2/HAc(M),\ NaCl\ (m)/AgCl/Ag$$

and 0.4644 the electromotive force of the cell

$$H_2/HCl(0.01)/AgCl/Ag$$

Then the electromotive force of the cell

$$H_2/HAc(M),\ NaCl(m)/AgCl/Ag/AgCl/HCl(0.01)/H_2$$

will be given by

$$E - 0.4644 = 0.05915 \log \frac{(0.904)^2\,(0.01)^2}{(\gamma_{HCl})^2\, m_H m}\text{, or}$$

$$16.9062\,E - 3.7636 + \log m + 2 \log \gamma_{HCl} = -\log m_H \qquad (1)$$

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[1] This paper represents a part of the thesis presented by Benton B. Owen to the Graduate School of Yale University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Harned and Robinson, THIS JOURNAL, 50, 3157 (1928).

if we take the activity coefficient of hydrochloric acid to be 0.904[3] at 0.01 molal concentration. γ_{HCl} is the activity coefficient of hydrochloric acid in the solution containing the undissociated acetic acid molecule at a molal concentration of $(M - m_{\mathrm{H}})$. When M is zero, γ_{HCl} becomes the activity coefficient of hydrochloric acid in pure, aqueous, sodium chloride solutions, and will be denoted $\gamma^{\circ}_{\mathrm{HCl}}$. The values of E for the weak acid–sodium chloride cells, and 0.4644 for the reference cell were obtained under identical experimental conditions, so that the double cell indicated does not include any experimental inconsistencies. It should also be remarked that our final results are independent of the choice of 0.904 as the activity coefficient of 0.01 M HCl. In Equation 1, as first written, the term γ_{HCl} is referred to 0.904 and enters the calculations only in a ratio with this reference value. Thus, at the start, the present method is considerably more advantageous than that employed by Cohn[4] and others in which their choice of this reference value influences the final values by several per cent. From Equation 1 we may write the identity

$$16.9062\,E - 3.7636 + \log m + 2\log \gamma^{\circ}_{\mathrm{HCl}} = -\log m_{\mathrm{H}} - 2\log \frac{\gamma_{\mathrm{HCl}}}{\gamma^{\circ}_{\mathrm{HCl}}} \qquad (2)$$

This is Equation 14a in Harned and Robinson's paper.[2] Since $\gamma^{\circ}_{\mathrm{HCl}}$ and not γ_{HCl} is known in salt solutions, our first step will be to drop the term containing γ_{HCl} in Equation 2, and define an unreal hydrogen-ion concentration, m'_{H}, by means of the equation

$$16.9062\,E - 3.7636 + \log m + 2\log \gamma^{\circ}_{\mathrm{HCl}} = -\log m'_{\mathrm{H}} \qquad (3)$$

m'_{H} would be the true hydrogen-ion concentration if $\gamma^{\circ}_{\mathrm{HCl}}$ was not changed to γ_{HCl} by the variation of the character of the medium caused by the addition of the undissociated molecule of the weak acid, HA. Since the activity coefficient of hydrochloric acid relative to unity at infinite dilution in water is affected considerably by this variation of the medium, the quantity m'_{H} will be designated throughout the following discussion as the "apparent hydrogen-ion concentration," which will serve to differentiate it from the true hydrogen-ion concentration. Later when we come to learn more of the effect of the medium on both m'_{H} and γ_{HCl}, we shall show how the true hydrogen-ion concentration may in all cases be computed.

By subtracting (3) from (2), we obtain

$$\log \frac{m'_{\mathrm{H}}}{m_{\mathrm{H}}} = 2\log \frac{\gamma_{\mathrm{HCl}}}{\gamma^{\circ}_{\mathrm{HCl}}} \qquad (4)$$

which relates the true and apparent hydrogen-ion concentrations. Harned and Robinson estimated approximately the right-hand member of Equation 4 by assuming that the variation of γ_{HCl} with M was the same for

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[3] Randall and Young, THIS JOURNAL, 50, 989 (1928).

[4] Cohn, *ibid.*, 50, 696 (1928).

water–acetic acid mixtures as for water–alcohol mixtures. As a part of this investigation it will be shown that this quantity may be determined accurately from the electromotive forces of the acetic acid-sodium chloride cells.

The thermodynamic equation for the dissociation of the acid is

$$K = \frac{\gamma_H \gamma_{Ac} m_H m_{Ac}}{\gamma_{HAc} m_{HAc}} = \gamma_A^2 \frac{m_H^2}{M - m_H} = \gamma_A^2 k \tag{5}$$

This equation is valid when γ_A equals unity at infinite dilution of electrolyte in a given solvent. Thus, k approaches K as the ionic strength becomes zero. Since our first computation yields the apparent hydrogen-ion concentration, m'_H, and not m_H, we must employ another set of quantities defined by

$$K = \frac{\gamma'_H \gamma'_{Ac} m'_H m'_{Ac}}{\gamma'_{HAc} m'_{HAc}} = \gamma'^2_A \frac{m'^2_H}{M - m'_H} = \gamma'^2_A k' \tag{6}$$

The primed quantities in this equation are all apparent values because of their relation with m'_H. Further, k' does not approach K as the ionic strength approaches zero nor does γ'_A approach unity under this condition. Consequently, the limiting value of these functions will be written k° and γ°_A. As a result we may write

$$K = \gamma_A^2 k = \gamma'^2_A k' = \gamma^{\circ 2}_A k^\circ \tag{7}$$

It should be noted here that γ_A corresponds to $\gamma_{(corr.)}$, the corrected activity coefficient, and γ'_A to γ_A in Harned and Robinson's paper.

The Extrapolation of k' to Infinite Dilution of Both Ions and Undissociated Acetic Acid Molecules.—If we take the logarithm of Equation 5, we obtain

$$\log K = 2 \log \gamma_A + \log k \tag{8}$$

For moderate concentrations, the activity coefficient of any uni-univalent electrolyte, referred to unity at infinite dilution in a given solvent, may be expressed as a function of the ionic strength by the semi-empirical equation

$$2 \log \gamma_A = -A \sqrt{\mu} + 2B\mu \tag{9}$$

The constant *A* is equal to unity for aqueous solutions, whence it will suffice for our purpose to combine Equations 8 and 9 to give

$$\log k - \sqrt{\mu} = \log K - 2B\mu \tag{10}$$

Thus, if we plot (log k $- \sqrt{\mu}$) against μ, a straight line should be obtained, and the intercept for $\mu = 0$ will be log K. Several investigators[5] have employed Equation 10 as a basis for similar extrapolations, but, as we have pointed out before, k' and not k is directly measurable. Furthermore, since m'_H and not m_H is used in calculating the ionic strength, the latter must be written μ' and not μ. In salt solutions of weak acids the

[5] Bjerrum and Unmack, *Det. Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*, 9, 1 (1929); Sihvonen, *Z. Electrochem.*, 36, 165 (1930).

difference between μ' and μ is very small and does not alter the plot appreciably. In practice, therefore $(\log k^{t} - \sqrt{\mu'})$ is plotted against μ', and although this plot is a straight line, the intercept is not log K, but is a quantity which we shall denote log k^{0}. From the definition of k and k', and Equation 7, we may write

$$\log \frac{k'}{k} = 2 \log \frac{\gamma_A}{\gamma'_A} = 2 \log \frac{m'_H}{ma} - \log \frac{M - m'_H}{M - ma} \tag{11}$$

Since for acids of the strength of acetic the last term on the right is less

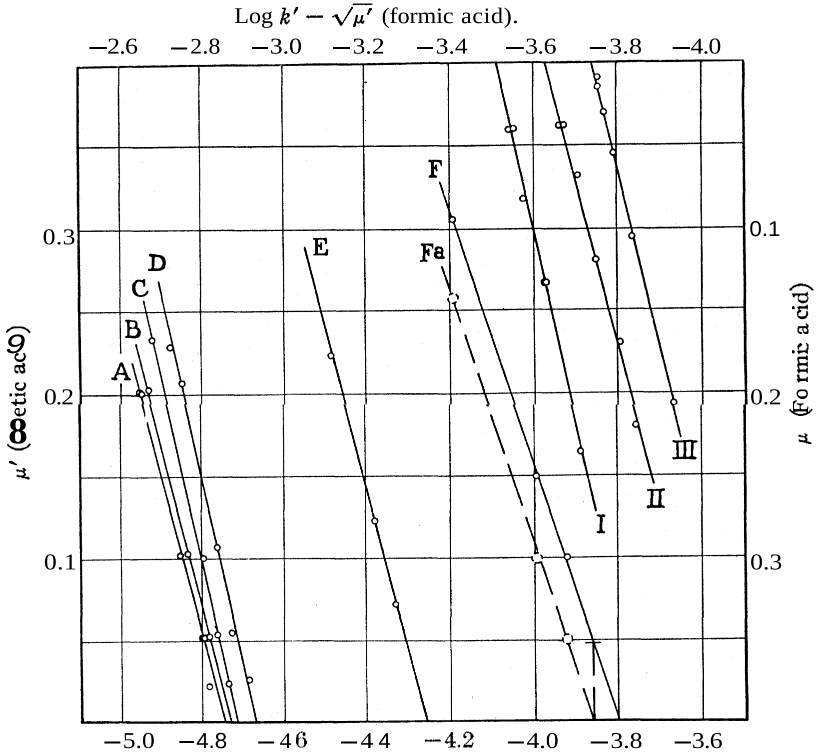

Fig. 1.—Acetic and formic acids in sodium chloride solutions. Molality of acetic acid: A, 0.1; B, 0.2; C, 0.52; D, 1.0; E, 5.41; F, 10.2. Molality of formic acid: I, 2.13; II, 1.0; III, 0.1.

than 0.0008 when M equals 5, it may be neglected. Consequently, rewriting Equation 11 and introducing Equation 4, we obtain

$$\log \frac{k'}{k} = 2 \log \frac{\gamma_A}{\gamma'_A} = 2 \log \frac{m'_H}{m_H} = 4 \log \frac{\gamma_{HCl}}{\gamma^{0}_{HCl}} \tag{12}$$

Further, by combining this equation with (7) and (10), we obtain

$$\log k' - \sqrt{\mu} = \left((\log k^{0} + 2 \log \gamma^{0}_A + 4 \log \frac{\gamma_{HCl}}{\gamma^{0}_{HCl}}\right) - 2B\mu \tag{13}$$

At zero ionic strength, 2 log (γ_A/γ'_A) becomes 2 log $1/\gamma^\circ_A$ by definition, whence by Equation 12

$$2 \log \gamma^\circ_A + 4 \log \frac{\gamma_{HCl}}{\gamma^\circ_{HCl}} = 0, \text{ when } \mu = 0 \tag{14}$$

Consequently, the bracketed member on the right of Equation **13** is log k°.

Since μ' may be written for μ without appreciable error, Equation 13 becomes

$$\log k' - \sqrt{\mu'} = \log k^\circ - 2B\mu' \tag{15}$$

Figure **1** shows the plot of (log $k' - \sqrt{\mu'}$) against μ' for various concentrations of acetic acid in sodium chloride solutions which has been drawn by the use of the data contained in Table I and from which it is obvious that straight lines are obtained.

TABLE I

THE APPARENT HYDROGEN-ION CONCENTRATIONS OF ACETIC ACID IN SODIUM CHLORIDE SOLUTIONS

M	m	$2 \log \gamma^\circ_{HCl}$	m_H	Log $k' - \sqrt{\mu'}$	d
0.10	0.0	....	0.0	(−47438)	0.0
.0997	.02	$\bar{1}$.8790	.001506	−4.7830	.0215
.0992	.05	$\bar{1}$.8306	.001617	−4.7992	.0516
.1003	.05	$\bar{1}$.8306	.001634	−4 7940	.0516
.0991	.1	$\bar{1}$.7906	.001692	−4.8509	.1017
.1004	.1985	$\bar{1}$.7552	.001764	−4.9483	.2003
.0991	.2	$\bar{1}$.7545	.001741	−4.9562	.2017
.20	.0	....	.0	(−4.7308)	.0
.1965	.05	$\bar{1}$.8300	.002335	−4.7806	.0523
.2018	.1	$\bar{1}$.7900	.002471	−4.8339	.1025
.2018	.2	$\bar{1}$.7542	.002570	−4.9294	.2026
.52	.0	....	.0	(−4.7156)	.0
.519	.02	$\bar{1}$.8738	.003675	−4.7359	.0238
.519	.05	$\bar{1}$.8285	.003901	−4 7614	.0539
.519	.0957	$\bar{1}$.7918	.004135	−4.7947	.0998
.519	.2285	$\bar{1}$.7481	.004337	−4.9197	.2328
1.00	.0	....	.0	(−4.6694)	.0
1.002	.01997	$\bar{1}$.8702	.005475	−4.6852	.0254
1.002	.049	$\bar{1}$.8324	.005666	−4.7256	.0547
1.002	.1	$\bar{1}$.7882	.006051	−5.7602	.1061
1.002	.2	$\bar{1}$.7536	.006352	−4.8466	.2064
1.002	.222	$\bar{1}$.7488	.006350	−4 8724	.2284
5.40	.0	....	.0	(−4.2552)	.0
5.41	.05	$\bar{1}$.8114	.02164	−4 3287	.0716
5.41	.1	$\bar{1}$.7800	.02245	−4.3793	.1225
5.39	.2	$\bar{1}$.7500	.02287	−4.4832	.2229
10.2	.0	....	.0	(−3.7970)	.0
10.2	.05	$\bar{1}$.7914	.05013	−3.9231	.1001
10.2	.0992	$\bar{1}$.7692	.04997	−3.9953	.1492
10.2	.257	$\bar{1}$.7378	.04825	−4.1921	.3053

The first two columns of the table are taken from Harned and Robinson's data. Column 3 contains the values of log $\overset{\circ}{\gamma}_{HCl}$ at the same ionic strength as that obtaining in the acetic acid–sodium chloride cells. These values were obtained from a plot of log $\overset{\circ}{\gamma}_{HCl}$[6] against $\sqrt{\mu}$ of the data given by Harned and Åkerlöf,[7] which have been recalculated to conform with the value 0.904 for 0.01 M hydrochloric acid in pure water. A trial value of $\overset{\circ}{\gamma}_{HCl}$ was used to compute an approximate value of m'_H, which was then employed to compute a more exact value of μ by which a final value of log $\overset{\circ}{\gamma}_{HCl}$ could be read from the plot. Column 4 contains the values of m'_H, calculated by Equation 3, and Columns 5 and 6 the corresponding values of the functions indicated. The quantities in parenthesis are the values of log $k°$ read from the plots in Fig. 1 for infinite dilution of ions. To obtain K it is now necessary to cross-extrapolate these values to infinite dilution of the acetic acid molecules. This can easily be accomplished since we find that $k°$ and K are related by

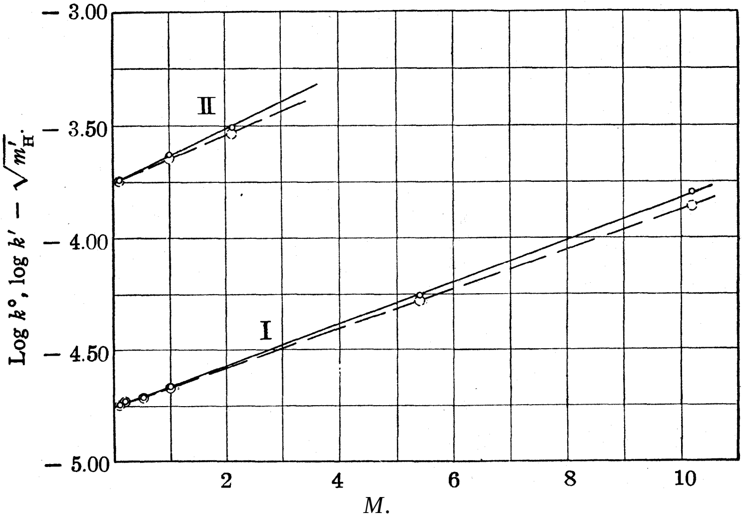

Fig. 2.—Extrapolation for log K. I, Acetic acid; II, formic acid.
——○——, log $k°$; — —○— —, log k' − $\sqrt{m'_H}$.

$$\log \frac{k°}{K} = 2SM \tag{16}$$

where S is an empirical constant which we shall call the medium effect, and M is molal concentration of the acetic acid. Figure 2 contains a plot

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[6] So long as m_H is of the order of 0.01 molal, or less, the values of the activity Coefficient of hydrochloric acid in salt solutions are practically independent of *r n* and depend only upon μ. Consequently, we have employed the 0.01 hydrochloric acid series throughout. This point was discussed in detail by Harned and Robinson.

[7] Harned and Åkerlöf, *Physik. Z.*, 27, 411 (1926).

of log k° against M. Since a straight line may be drawn through the points, Equation 16 is confirmed. From this plot we find that for acetic acid S equals 0.047 and log K equals –4.758, whence K equals 1.75 X 10^{-5} at 25°.

The Effect of Change of Solvent upon the Quantities under Consideration.—According to Equation 16, we found that log k°/K, the value of log (k'/k) extrapolated to zero ionic strength, varies linearly with the concentration of the weak acid. If *we* ***make*** *the important hypothesis that this effect of the medium due to the undissociated acid maintains at all ionic strengths or is independent of the electrolyte concentrations,* we may combine Equations 12 and 16 and obtain

$$2SM = \log \frac{k^{o}}{K} = 2 \log \frac{1}{\gamma^{\circ}_{A}} = \log \frac{k'}{k} = 2 \log \frac{\gamma_{A}}{\gamma'_{A}} = 2 \log \frac{m'_{H}}{m_{H}} = 4 \log \frac{\gamma_{HCl}}{\gamma^{\circ}_{HCl}} \qquad (17)$$

From the parallel nature of the plots in Fig. 1 and the character of the results obtained by the application of this hypothesis, we regard it as a very close approximation. Upon the basis of this hypothesis, Equation 17 immediately allows the calculation of the true hydrogen-ion concentration and the true activity coefficient of acetic acid in sodium chloride solutions from the data in Table I. It also furnishes an evaluation of γ_{HCl}, the activity coefficient of hydrochloric acid in sodium chloride solutions containing undissociated molecules of acetic acid. Since Equation 17 summarizes the connection between the medium effect and all the thermodynamic quantities under consideration, we shall summarize the approximations involved. Reading from left to right, we shall consider each sign of equality in turn. The first equality is empirical and is justified by Fig. 2. The second is definitional and follows from Equation 7. The third involves the hypothesis that the medium effect is independent of the presence of ions. The fourth and sixth equalities are definitional, and the fifth involves neglecting the small term, log $(M-m'_{H})/$-$(M-m_{H})$, which, however, may be retained, as in Equation 11, if the accuracy of the data would seem to justify this complication.

Properties of the Salt-Free Acetic Acid Solutions, and an Alternate Extrapolation for K.—The dotted line, Fa, in Fig. 1 near that for 10.2 M acetic acid is the plot of (log k' – $\sqrt{\mu'}$) against m, the sodium chloride concentration. If this is assumed to be straight, its intercept is nearly equal to (log k' – $\sqrt{m'_{H}}$) for 10.2 acetic acid in pure water. A more exact value may be obtained from the equation

$$2 \log m'_{H} = R + \sqrt{m'_{H}} + \log (M-m'_{H}) \qquad (18)$$

in which R equals (log k' – $\sqrt{m'_{H}}$). Approximate values of R and m'_{H}-$(= \mu')$ are read from the plot, substituted in the right side of Equation 18 and solved for a more exact value of m'_{H}, which in turn is used to read a more exact value of R from the plot. By repetition of this process until

Equation 18 is satisfied, exact values of R and m'_{H} may be obtained. These are given in Table II together with the true values of m_{H} and log γ_{A} calculated by Equation 17. The noticeable irregularity of these values of log γ_{A} is due to the fact that they represent the difference of two relatively large quantities and include the experimental discrepancy between the experimental points and the straight line in Fig. 2. Figure 2 also contains the plot of (log $k' - \sqrt{m'_{\mathrm{H}}}$) against M, shown as large circles through which a straight line (dashed) extrapolates to log K. This value of K is almost exactly 1.75 X 10^{-5} and thus corresponds very closely to that obtained by means of the log k^{o}, M plot.

TABLE II

THE APPARENT AND REAL HYDROGEN-ION CONCENTRATIONS OF *M* ACETIC ACID IN PURE WATER

M	R	m'_{H}	m_{H}	Log γ_{A}
0.0	(−4.7580)	0.0	0.0	0.0
.1	−4.7452	.001390	.001375	− .0204
.2	−4.7330	.002015	.001972	− .0256
.52	−4.7186	.003356	.003173	− .0243
1.0	−4.6740	.004985	.004474	− .0303
5.41	−4.2758	.01988	.01107	− .0574
10.2	−3.8600	.04820	.01598	− .0794

Measurements of Cells Containing Formic Acid in Sodium and Potassium Chloride Solutions at 25°.—The electrodes, cells and technique employed in these measurements were the same as described by Harned and Robinson. Table III contains the data. The significance of the various quantities is obvious from the previous discussion of acetic acid. Column 2 gives the observed electromotive force corrected to one atmosphere pressure of hydrogen and divided by 0.05915. All cells which attained equilibrium are included in the table. The electromotive forces of the entire 0.1 M formic acid series in potassium chloride and above 0.025 for m in the sodium chloride solutions are the means of duplicate cells. The average deviation of the individual values from the mean was about 0.04 millivolt for the latter and 0.09 for the former. The data for more concentrated formic acid solutions were obtained with somewhat less care since they were intended only to determine the value of the medium effect.

Figure 1 contains the plot of (log $k^{t} - \sqrt{\mu'}$) against μ', and the extrapolated values of log k° are given in parentheses in Table III, Column 5. The curve for 0.1 M formic acid in sodium chloride solutions, for which the highest accuracy is claimed, gives striking confirmation of the validity of Equation 15 up to $\mu' = 0.2$. The data for 0.1 M formic acid in potassium chloride solutions are not included in Fig. 1 since it extrapolates to the same value of log k° as the corresponding sodium chloride curve,

TABLE III

THE APPARENT HYDROGEN-ION CONCENTRATION OF FORMIC ACID IN POTASSIUM AND SODIUM CHLORIDE SOLUTIONS

0.10031 **Formic Acid, *m* Potassium Chloride**

m	$\frac{E}{0.05915}$	$2 \text{ Log } \gamma^{\circ}_{HCl}$	m'_H	$\text{Log } k' - \sqrt{\mu'}$	m_H	$\text{Log } \gamma_A$
	.....	....	0.0	(−3.7413)	0 0	0.0
0 05	7.53339	$\bar{1}.8228$	.005110	−3.7965	.005048	− .0897
.1	7.25630	$\bar{1}.7807$	.005329	−3.8489	.005264	− .1084
.2	6.97667	$\bar{1}$ 7398	.005573	−3.9377	.005505	− .1285
5	6.61420	$\bar{1}.7076$	.005531	−4.2021	.005464	− .1251
1 0	6.32291	1.7134	.005337	−4.5257	,005274	− .1091
1.5	6.14505	$\bar{1}$ 7413	.005026	−4.8034	.004965	− .0823
2 0	6.01369	$\bar{1}.7800$	.004666	−5 0587	.004609	− .0492
3.0	5.80423	$\bar{1}$ 8700	.004095	−5.4918	.004046	,0088
0.10031 **Formic Acid, *m* Sodium Chloride**						
	.....	....	0.0	(−3.7413)	0.0	0.0
0 005	8.48690	$\bar{1}.9147$	.004603	−3.7530	.004547	− .0431
.01	8.19358	$\bar{1}.8966$	.004714	−3.7550	004657	− .0538
.025	7.81234	$\bar{1}.8616$	.004918	−3.7689	.004858	− .0727
.05	7.52713	$\bar{1}.8269$	.005136	−3.7921	.005073	− .0920
.1	7.24277	$\bar{1}.7884$	.005401	−3.8370	.005336	− .1145
.2	6.95909	$\bar{1}.7537$	.005621	−3.9302	.005553	− .1323
.5	6.57346	$\bar{1}.7287$	.005788	−4.1617	.005717	− .1454
1.0	6.24937	$\bar{1}.7694$	.005558	−4.4896	.005490	− .1272
1.5	6.03686	$\bar{1}.8285$	.005275	−4.7604	.005211	− .1039
2.0	5.86695	$\bar{1}.9008$	,004953	−5.0056	.004893	− .0758
3.0	5 58445	0.0740	.004247	−5.4595	.004196	− .0075
1.000 **Formic Acid, *m* Sodium Chloride**						
	.....	....	0.0	(−36300)	0.0	0.0
0.02	7.3508	$\bar{1}.8480$	.01836	−3.6602	.01604	− .0858
.02	7.3569	$\bar{1}.8484$	.01808	−3.6726	.01581	− .0793
.05	6.9772	$\bar{1}.8133$	.01880	−3.7059	.01413	− .0962
.1	6 6877	$\bar{1}.7814$	.01970	−3.7484	.01722	− .1168
.15	6.5263	$\bar{1}.7624$	.01990	−3.8059	.01739	− .1211
.2	6 4045	$\bar{1}.7504$	,02031	−3.8451	.01775	− .1302
2.1253 **Formic Acid, *m* Sodium Chloride**						
	.....	....	0 0	(−3.5100)	0.0	0.0
.01	7.4350	$\bar{1}.8448$	,03047	−3.5546	.02288	− .0754
.01	7.4284	$\bar{1}.8440$	.03099	−3.5411	.02328	− .0829
.05	6.7464	$\bar{1}.8024$	.03280	−3.5769	.02463	− .1076
.1	6.4573	$\bar{1}.7750$	.03399	−3.6238	.02553	− .1232
.1	6.4585	$\bar{1}.7750$	.03389	−3.6261	.02546	− .1221
.2	6.1677	$\bar{1}.7480$	.03523	−3.7114	.02646	− .1389

and diverges too slightly (to the right of Curve III) to be clearly distinguished on the scale used.

The fact that the value of log k° is thus apparently independent of the salt used in the solutions of finite ionic strength is obviously an indication in favor of the assumption leading to Equation 17, but much stress should not be laid upon this point since high accuracy is not claimed for the potassium chloride series, and exact agreement must depend on the values for γ°_{HCl} in sodium and potassium chloride solutions given by Harned and Åkerlöf.

Curve II in Fig. 2 shows the extrapolation for log K for formic acid. The extrapolation represented by Equation 16 is shown by the solid line and leads to the values of 0.0585 and -3.753 for S and log K, respectively. K therefore equals 1.77×10^{-4} at 25°.

The dashed line is based upon values of m'_H equal to 0.004482, 0.01732 and 0.03015 in 0.1, 1 and 2.13 M salt-free formic acid solutions, respectively, and extrapolates to approximately the same value of log K. From the value of S for formic acid and Equation 17, the true values of the hydrogen-ion concentrations and activity coefficients have been calculated from the apparent values, and included in Table III, Columns **6** and 7.

The values for γ_A for the 0.1 M formic acid–sodium chloride series may be expressed by the same type of equation, which holds for a strong electrolyte in similar solutions. Thus, the equation

$$\log \gamma_A = -\frac{0.5\sqrt{\mu}}{1 + 1.175\sqrt{\mu}} + 0.095\,\mu \qquad (19)$$

is valid up to an ionic strength of 3 to within a maximum deviation of 1.75% and an average deviation of 0.85%. Since the dielectric constant of 0.1 M formic acid is not appreciably different from that of water, we have retained the universal constant of 0.5 derived from the Debye and Hückel theory. This calculation shows that by employing the definition of the ionic activity coefficient of a weak electrolyte which Harned has applied to water, and Harned and Robinson to weak acids and bases, we arrive at the conclusion that these quantities may be numerically and theoretically treated by the same methods that were used in the cases of strong electrolytes.

The Dissociation Constants of Some Weak Bases.—By employing the data of Harned and Robinson on the methylamines and ammonia in aqueous sodium chloride solutions, we can determine only one value of k° for each base. In order to calculate the true dissociation constants, K, from k° we have shown that it is necessary to know the values of the medium effects, S, which require additional data for at least two concentrations of base. Even though exact values of S are unknown, our method of extrapolation can be shown to be applicable to solutions of these bases. In Table IV are shown the values of m'_{OH} determined by Harned and Robinson, and the values of μ' and ($\log k' - \sqrt{\mu'}$) calculated therefrom. These latter are plotted in Fig. **3.** Since, on account of the experimental difficulties, the points at high dilution are scattered, it was impossible

TABLE IV

THE EXTRAPOLATION FUNCTIONS FOR WEAR BASES IN SODIUM CHLORIDE SOLUTIONS

0 5030 *M* NH_3, NaCl (*m*)			0.1987 $(CH_3)_2NH$, NaCl (*m*)		
m		log $k' - \sqrt{\mu'}$	*m*	m'_{OH}	log $k' - \sqrt{\mu'}$
0.0	**0.0**	(−4.700)	0.0	0.0	(−3.265)
.1	.004382	−4.738	.02	.01178	−3.308
2	.004683	−4.809	.05	,01273	−3.310
.5	.005159	−4.983	.1	.01403	−3.310
1	.005621	−5.200	.2	.01620	−3.307
1.5	.005776	−5.400	.5	.01879	−3.428
0.1989 CH_3NH_2, NaCl (*m*)			1	.02204	−3.572
0.0	0.0	(−3.340)	1.5	.02410	−3.713
.02	.01098	−3.369	0.1891 $(CH_3)_3N$, NaCl (*m*)		
05	.01191	−3.369	0.0	0.0	(−4.245)
.1	.01293	−3.383	.1	.004502	−4.283
.2	.01431	−3.418	.2	.005080	−4.306
.5	.01665	−3.537	.5	.006268	−4.379
1	.01857	−3.728	1	.007296	−4.537
1.5	01984	−3.890	1.5	,008136	−4.665

to determine values of log k° by depending only on the points below 0.3 . Consequently, the data were plotted to about 1.5μ' and the extrapo-

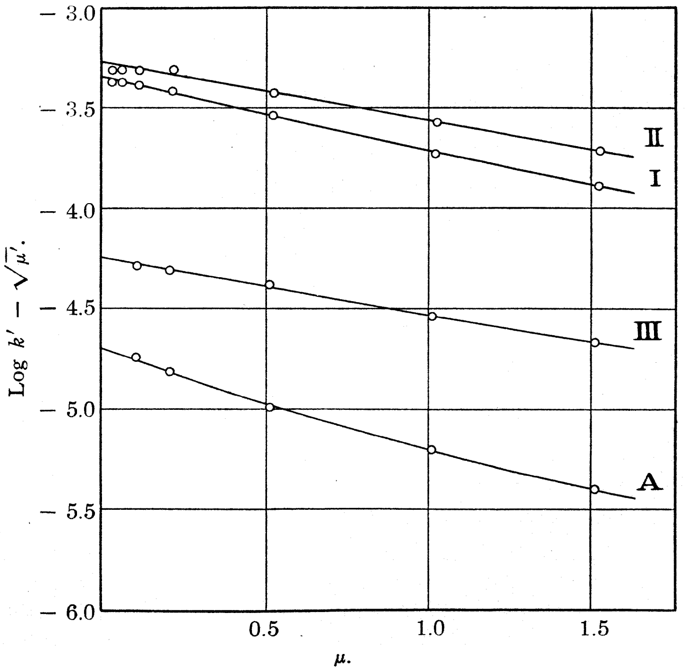

Fig. 3.—Weak bases in sodium chloride solutions. **A,** 0.503 M NH_3; I, 0.199 M $NH_2(CH_3)$; II, 0.199 M $NH(CH_3)_2$; III, 0.189 M $N(CH_3)_3$.

lation was accomplished by the use of long curves in such a way that a straight line was approached at dilute ionic strengths. The values of log k° so obtained are included in Table IV in parentheses. The corresponding values of k° are shown in Table V and compared with the accepted values of K calculated from conductivity measurements. Disregarding for the moment the trimethylamine solutions, our values of k° are all slightly higher than those of K, and our experience with the medium effect would lead us to expect this according to Equation 16. In the absence of sufficient data to evaluate S exactly, we have assumed that the value of 0.047 for S, previously found for acetic acid, is applicable to each basic solution and have calculated the corresponding values of K. These are included in Table V and agree satisfactorily with those derived from conductivity data except in the case of trimethylamine. In this case we believe the discrepancy is considerably greater than the experimental error of the measurements, or in the estimation of the medium effect. It should be mentioned that the medium effect must in all probability be intimately connected with the difference between the dielectric constants of water and the weak electrolyte, and since acetic acid and the bases under consideration have dielectric constants of approximately the same magnitude, our assumption of equality of medium effect is logical. Indeed, for the particular concentrations with which we are dealing, an error of 50% in the assumed value of S would only cause an error of 4.3% in K in the cases of the amines, and of 10% for ammonia.

TABLE V

DISSOCIATION CONSTANTS OF WRAK BASES $\times 10^{-5}$

Source	NIL	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
"Int. Crit. Tables," Vol. VI	**1 81**	40.0	50.0	6.50
This paper (K)	**1.79**	**43.8**	52.0	5.45
This paper (k°)	2.00	45.7	54.3	5 69

Conclusions and Summary

1. By the use of the extrapolation function. (log k' $- \sqrt{\mu'}$), we have evaluated the dissociation constants of acetic and formic acids from measurements of cells without liquid junction. This method is thermodynamically sound, and employs no extra-thermodynamical postulates. The accuracy of the numerical values obtained depends entirely upon the validity of the empirical extrapolation function used, and the accuracy of the experimental data.

2. By means of Equation 17, the hydrogen-ion concentrations and ionic activity coefficients may be computed in aqueous solutions containing both the weak acid and salts at various concentrations. The logarithm of the activity coefficients of these electrolytes, referred to unity at infinite dilution in water, varies linearly with the weak acid concentration according to the law expressed by Equations 16 and 17. This law is valid at zero

ionic strength and, further, we believe that it is valid, or very nearly so at all salt concentrations. This latter statement may be verified by computing the activity coefficients relative to unity in a given solvent at various concentrations of the undissociated acid molecule. The results thus obtained agree reasonably with what is to be expected according to the Debye and Hückel theory. Since Harned and Robinson considered this matter, we have not considered it in detail in the present investigation.

3. Our value of 1.75×10^{-5} for the dissociation constant of acetic acid agrees closely with 1.785×10^{-5}, recently computed by Davies[8] by applying viscosity corrections to the conductivity data of Kendall.[9] On the other hand, our value of 1.77×10^{-4} for formic acid is considerably lower than 1.87×10^{-4} obtained by Davies with an extrapolation of Auerbach and Zeglin's[10] conductivity data at 18°.

4. Values for the dissociation constants of ammonia, and the mono-, di- and trimethylamines were computed by the same method from Harned and Robinson's data, and compared with those recently compiled.

5. The present investigation, following that of Harned and Robinson, demonstrates how it is possible, from measurements of cells without liquid junction, to evaluate the thermodynamic behaviors of weak acids and bases in salt solutions, and to determine their dissociation constants by a method which is thermodynamically exact.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

THE ACID AND BASE CONSTANTS OF GLYCINE FROM CELLS WITHOUT LIQUID JUNCTION[1]

BY HERBERT S. HARNED AND BENTON B. OWEN

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In this study of aqueous solutions of glycine, we shall assume with Bjerrum[2] that the neutral ampholyte molecule in solution exists as "zwitterion," to be designated hereafter "amphion," but our numerical results do not depend upon the validity of this assumption. We further assume complete dissociation of sodium glycinate and glycine hydrochloride in the solutions with which we are concerned, thus

$$ClNH_3CH_2COOH \longrightarrow Cl^- + {}^+NH_3CH_2COOH, \text{ and}$$
$$NH_2CH_2COONa \longrightarrow Na^+ + NH_2CH_2COO^-$$

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[8] Davies, *Phil. Mag.*, [7] 4,244 (1927).

[9] Kendall, *J. Chem. Soc.*, 101,1285 (1912).

[10] Auerbach and Zeglin, *Z. physik. Chem.*, 103, 191 (1923).

[1] This paper represents part of the dissertation presented by Benton B. Owen to the Graduate School of Yale University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Bjerrum, *Z. physik Chem.*, 104,147 (1923).

or if the sodium glycinate be hydrated

$$HONH_3CH_2COONa \longrightarrow Na^+ + HONH_3CH_2COO^-$$

The amphcation and amphanion being weak electrolytes, their incomplete dissociation may be represented by

$$\begin{aligned} {}^+NH_3CH_2COOH &\rightleftharpoons {}^+NH_3CH_2COO^- + H^+, \text{ and} \\ H_2O + NH_2CH_2COO^- &\rightleftharpoons {}^+NH_3CH_2COO^- + OH^-, \text{ or} \\ HONH_3CH_2COO^- &\rightleftharpoons {}^+NH_3CH_2COO^- + OH^- \end{aligned}$$

For reasons of simplicity we shall hereafter write G^- for the amphanion. $NH_2CH_2COO^-$, Z^* for the amphion, ${}^+NH_3CH_2COO^-$, ZOH^- for the hydrated amphanion, $HONH_3CH_2COO^-$, and ZH^+ for the amphcation, ${}^+NH_2CH_2COOH$ The above equations then become

$$\begin{aligned} ClZH &\longrightarrow Cl^- + ZH^+ && (1) \\ NaG &\longrightarrow Na^+ + G^- && (2) \\ NaZOH &\longrightarrow Na^+ + OH^- && (2a) \end{aligned}$$

and

$$\begin{aligned} ZH^+ &\rightleftharpoons Z^\pm + H^+ && (3) \\ H_2O + G^- &\rightleftharpoons Z^\pm + OH^- && (4) \\ ZOH^- &\rightleftharpoons Z^\pm + OH^-, \text{ and} && (4a) \\ H_2O + G^- &\rightleftharpoons ZOH^- && (5) \end{aligned}$$

The exact thermodynamic equations for the acid and base equilibria in water, in the absence of any effect upon the medium due to the presence of glycine, we represent by

$$K_A = \frac{\gamma_{Z\pm}\ \gamma_{H^+}}{\gamma_{ZH^+}} \frac{m_{Z\pm}\ m_{H^+}}{m_{ZH^+}} = \gamma_A{}^2\, k_A \qquad (6)$$

$$K_B = \frac{\gamma_{Z\pm}\ \gamma_{OH^-}}{\gamma_{G^-}\ a_{H_2O}} \frac{m_{Z\pm}\ m_{OH^-}}{m_{G^-}} = \gamma_B{}^2\, k_B, \text{ or} \qquad (7)$$

$$K_B = \frac{\gamma_{Z\pm}\ \gamma_{OH^-}}{\gamma_{ZOH^-}} \frac{m_{Z\pm}\ OH^-}{m_{ZOH^-}} = \gamma_{Bh}{}^2\, k_{Bh}, \text{ and} \qquad (7a)$$

$$K_h = \frac{\gamma_{ZOH^-}}{\gamma_{G^-}\ a_{H_2O}} \frac{m_{ZOH^-}}{m_{G^-}}. \qquad (8)$$

The "γ's" are the activity coefficients, and the "m's" the molal concentrations of the species denoted by the subscripts. K_h is the equilibrium constant for the hydration of the glycinate ion, and K_A and K_B are the dissociation constants defined by Bjerrum for glycine as acid and base, respectively. k_A, and k_B or k_{Bh}, are the concentration terms in these constants, and γ_A, and γ_B or γ_{Bh}, the corresponding activity coefficients

$$\sqrt{\frac{\gamma_{Z\pm}\ \gamma_{H^+}}{\gamma_{ZH^+}}},\quad \sqrt{\frac{\gamma_{Z\pm}\ \gamma_{OH^-}}{\gamma_{G^-}\ a_{H_2O}}} \quad \text{or} \quad \sqrt{\frac{\gamma_{Z\pm}\ \gamma_{OH^-}}{\gamma_{ZOH^-}}}$$

Now in the measured solutions some neutral glycine is always present in varying amounts. This alters the properties of the medium, the dielectric constants for example,[3] and, therefore, influences the activity coefficients. This "medium effect" has been examined in some detail in a pre-

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[3] Neutral glycine increases the dielectric constant of water [Fürth, *Ann. Physik,* **70,** 63 (1923)].

vious communication by the authors,[4] and will be referred to later in this paper, so for the present it will only be necessary to state that our measurements yield "apparent" values of the concentrations and activity coefficients defined by the equations

$$K_A = \frac{\gamma'_{Z\pm}\ \gamma'_{H^+}}{\gamma'_{ZH^+}}\ \frac{m'_{Z\pm}\ m'_{H^+}}{m'_{ZH^+}} = \gamma'^2_A k'_A \tag{6'}$$

$$K_B = \frac{\gamma'_{Z\pm}\ \gamma'_{OH^-}}{\gamma'_{G^-}\ a'_{H_2O}}\ \frac{m'_{Z\pm}\ m'_{OH^-}}{m'_{G^-}} = \gamma'^2_B k'_B, \text{ or} \tag{7'}$$

$$K_B = \frac{\gamma'_{Z\pm}\ \gamma'_{OH^-}}{\gamma'_{ZOH^-}}\ \frac{m'_{Z\pm}\ m'_{OH^-}}{m'_{ZOH^-}} = \gamma'^2_{Bh} k'_{Bh}, \text{ and} \tag{7a'}$$

$$K_h = \frac{\gamma'_{ZOH^-}}{\gamma'_{G^-}\ a'_{H_2O}}\ \frac{m'_{ZOH^-}}{m'_{G^-}} \tag{8'}$$

It is important to note that the present investigation does not enable us to differentiate between the hydrated and unhydrated amphanion. We obtain numerical values for a "γ" which may be either γ_B or γ_{Bh}, and a "k" which may be either k_B or k_{Bh}. This is another illustration of the fact that thermodynamics alone does not yield information regarding the nature of the species present or the process taking place. Therefore, for reasons of convenience, we shall employ Equations 6, 7, 6' and 7' and keep the mathematical expressions in formal agreement with those of Bjerrum.

The "medium effect" is a function of the concentration, M, of the weak electrolyte causing a variation in the medium, and its evaluation requires the study of a series of apparent concentrations for several values of M. In this first study of ampholytes by cells without liquid junction, time restricted the measurements to one value of M only, and for this value we selected 0.1. This concentration is high enough to prevent certain experimental difficulties with the electrodes, and small enough to involve only a very small medium effect (probably of the order of 1%). Although we cannot evaluate the small medium effect in this research, we will consistently employ equations which take it into account (primed equations), so that this preliminary paper may serve both as an illustration of the method, and as an exact basis for a more detailed investigation, now under way, concerning the medium effect in glycine solutions.

Experimental Procedure

The cell measurements involved the use of 0.1 molal solutions of glycine hydrochloride, sodium glycinate and sodium hydroxide. Although alkaline solutions of glycine are relatively stable toward boiling, they are rapidly decomposed by oxygen in the presence of finely divided copper.[5] Because of the platinum black on the hydrogen electrodes, it was considered necessary to remove all traces of oxygen from the solutions

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[4] Harned and Owen, THIS JOURNAL. 52, 6079 (1930).

[5] Traube and Schönewald, Ber., 39, 184 (1906).

during their preparation, and to take every precaution to exclude contact with air during transfer to the cells. An approximately molal solution of sodium hydroxide was prepared by decanting sufficient saturated sodium hydroxide into a flask of thoroughly boiled distilled water, cooled in a stream of hydrogen, and kept thereafter under a pressure of this gas slightly above atmospheric. The solution was standardized against molar hydrochloric acid by means of a 500-cc. weight buret fitted with stopcocks allowing it to be filled and used in an atmosphere of hydrogen only. Next, a six-liter pyrex flask was fitted with a siphon tube bearing a three-way stopcock, an inlet tube with stopcock and a short filling tube bearing a 5-mm. bore stopcock through which the tip of the weight buret could be thrust against a stream of escaping hydrogen. Thirty-five grams of dry ammonia-free glycine was weighed into this flask with sufficient water to make the solution 0.1 molal in sodium glycinate (allowance being made for the water to be added later with the alkali). The glycine solution was boiled and cooled in a stream of pure hydrogen, and kept under a slight pressure of this gas. The boiling was done before the alkali was added to avoid the remote possibility that there might be some decomposition before the last traces of oxygen were removed. Then, by an approximate calibration of the weight buret, the calculated amount of sodium hydroxide solution was delivered into the flask through the large bore stopcock against a brisk counter current of hydrogen. Several weighings were necessary as the last few tenths of a cc. were added, but no air came in contact with the solutions during the manipulations. Since the flask had been tared, the weight of water lost during boiling was calculable, and an equal amount of water, previously boiled and cooled in hydrogen, was admitted through the large stopcock. A similar six-liter flask was fitted up, and in it was prepared an oxygen-free 0.1 molal solution of sodium hydroxide in the manner just described. This solution was to serve as reference solution in one side of the amalgam double cells. Since the same cells and technique are to be employed later with the glycine hydrochloride cells, the 0.1 molal glycine hydrochloride solution was prepared from glycine and molar hydrochloric acid solution in a manner similar to the sodium glycinate solution.

The addition of known amounts of salt to portions of the sodium glycinate solution was carried out in the following manner, and this method also applies *mutatis mutandis* to the glycine hydrochloride solution. Pure dry sodium chloride was weighed into 200-cc. solution flasks fitted with intake and delivery tubes bearing stopcocks. The flasks were then warmed and alternately evacuated and filled with hydrogen to remove the last traces of air, and finally filled with hydrogen. The delivery tube of the flask was then connected to the siphon tube of the sodium glycinate storage flask through a T-tube arranged so that it could be alternately evacuated and filled with hydrogen, thus permitting transfer of solution without the slightest contamination with air. The amount of solution received by the solution flask was then determined by weighing, and the molality of the sodium chloride calculated. The reference solution of 0.1 molal sodium hydroxide was transferred in a similar manner to solution flasks containing no salt.

The amalgam cells employed were of the usual type described by Harned[6] and Åkerlöf[7] except for minor alterations, and a slight reduction in size. In operation each cell contained about 75 cc. of solution, and each bubble tube about 25 cc. Before filling the cells they were fitted with solid rubber stoppers, and connected to the bubble tubes and solution flasks with thick rubber tubing, wired in place. Then the cells, bubble tubes and connections together were alternately exhausted and filled with hydrogen, and finally exhausted, so that when the stopcocks to the solution flasks were opened, the solutions were drawn into cells and bubble tubes containing traces of hydrogen and water vapor only. At this point the cells contained more solution than needed, so the

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[6] Harned, THIS JOURNAL, 47, 676 (1925).

[7] Åkerlöf, *ibid.*, 48, 1160 (1926).

excess was made to serve the purpose of excluding air while the limbs of the amalgam droppers and hydrogen electrodes were being substituted for the solid rubber stoppers closing the cells. Thus, while this replacement was being quickly made, the pressure of hydrogen from a bubble tube was forcing excess solution out of a cell between the rim and a stopper bearing an electrode, so that the time of simultaneous contact between electrode, air and solution was quite negligible. The amalgam droppers were fitted similarly.

The flow of hydrogen through the cells was begun immediately, and continued at the rate of about three bubbles per second for two or three hours before the flow of amalgam was begun. The droppers contained about 30 cc. of amalgam and required about six minutes to empty. The potentiometer was read thirty seconds after the flow of amalgam was begun, and then two or three times per minute thereafter. In general, the readings increased slightly during the first two or three readings, and then decreased steadily. The difference between the maximum and minimum readings varied roughly in an inverse manner with the salt concentration. Thus, for cells with zero salt concentration, the variation was 0.3 to 0.5 millivolt, while for 2 molal salt the difference was less than 0.1 millivolt.

The Determination of the Dissociation Constant and Activity Coefficient of Glycine as Base.—The electromotive force of the cell

$$H_2/NaOH(0.1)/Na_xHg/NaG(0.1),\ NaCl_{(m)}/H_2 \qquad (I)$$

at 25° is given by

$$E = 0.05915 \log \frac{(0.766)^2\,(0.1)^2\,a_{H_2O}}{(\gamma_{NaOH})^2\,(m + 0.1)\,m_{OH}\,a_{H_2O(0.1)}} \qquad (9)$$

where $a_{H_2O(0.1)}$ is the activity of water in 0.1 M sodium hydroxide, and a_{H_2O} is its activity in the sodium glycinate–chloride solution; 0.766 is the value of the activity coefficient of 0.1 M sodium hydroxide given by Harned and Åkerlöf.[8] It is important to note that our final results are independent of this choice of reference value. We shall let $a_{H_2O(0.1)}$ equal unity, and write Equation 9 as

$$16.9062\,E + 2.2315 + 2 \log \frac{\gamma_{NaOH}}{\sqrt{a_{H_2O}}} + \log p = -\log m_{OH} \qquad (10)$$

by which m_{OH} can be evaluated if we know $\gamma_{NaOH}/\sqrt{a_{H_2O}}$, the activity coefficient of sodium hydroxide in sodium glycinate–chloride solutions. This we do not know, but $\overset{\circ}{\gamma}_{NaOH}/\sqrt{\overset{\circ}{a}_{H_2O}}$, the activity coefficient of sodium hydroxide in sodium chloride solutions has been determined by Harned.[9] Substituting this value in Equation 10 we can calculate an apparent (unreal) hydroxyl-ion concentration defined by

$$16.9062\,E + 2.2315 + 2 \log \frac{\overset{\circ}{\gamma}_{NaOH}}{\sqrt{\overset{\circ}{a}_{H_2O}}} + \log p = -\log m'_{OH} \qquad (10')$$

and anticipated in Equations 6' and 7'. Values[10] of $\overset{\circ}{\gamma}_{NaOH}/\sqrt{\overset{\circ}{a}_{H_2O}}$ were

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[8] Harned and Åkerlöf, *Physik. Z.*, 27, 411 (1926).

[9] Harned, This Journal, 47, 648 (1925).

[10] So long as m_{OH} is of the order of 0.01 molal or less, the values of the activity coefficient of sodium hydroxide in salt solutions are practically independent of m_{OH} and depend only upon μ. Consequently, we have employed the 0.01 sodium hydroxide series throughout.

recalculated from the data of Harned[9] to conform to the value 0.901, given by Harned and Åkerlöf,[8] for the activity coefficient of 0.01 molal sodium hydroxide in pure water. Table I contains these values at corresponding values of μ read from a plot. The electromotive force, E, is the mean of all the readings made on each cell while the amalgam was flowing, and differs only slightly from the weighted average, using only readings of greatest constancy, or the graphical average from a plot of e. m. f. against time. In the particular case of the cell for which $m = 0$, E is the mean of the "E's" of four such cells, which were 0.09771, 0.09713, 0.09713 and 0.09840. This illustrates the poor agreement at lowest salt concentrations. The values of m'_{OH} were calculated by Equation 10′, of log k'_{B} by the relation $\log k'_{\text{B}} = 2 \log m'_{\text{OH}} - \log (0.1 - m'_{\text{OH}})$ which follows from (7'). The value of log k'_{B} given in parentheses was obtained by extrapolation to infinite dilution of electrolyte, and is therefore log $\overset{\circ}{k}_{\text{B}}$, where $\overset{\circ}{k}_{\text{B}}$ is the apparent basic dissociation constant of glycine. Obviously, $\overset{\circ}{k}_{\text{B}}$ must differ from the real dissociation constant, K_{B}, because its calculation involves extrapolation with a line whose slope is a function of the specific properties of both sodium chloride and sodium glycinate, through the region $\mu = \text{M}$ to $\mu = 0$, in which sodium glycinate alone is present. The same kind of difficulty is encountered in the calculation of activity coefficients of slightly soluble substances by extrapolation of solubility data in salt solutions. K_{B} equals $\overset{\circ}{k}_{\text{B}}$ in the experimentally unrealizable case in which $\text{M} = 0$, or, as we have shown in our previous paper, K_{B} can be evaluated exactly by extrapolation of values of $\overset{\circ}{k}_{\text{B}}$ corresponding to several different values of M. In Fig. 1 (I) are plotted as plain circles the values of log k'_{B} against the ionic strength. The equation of the straight line drawn through the points is

TABLE I

THE THERMODYNAMIC PROPERTIES OF SODIUM GLYCINATE SOLUTIONS

0.1 Molal sodium glycinate, m molal sodium chloride. Amalgam electrodes (approximately 0.1% Na).

$\mu = 0.1 + m$	E	$2 \log \frac{\overset{\circ}{\gamma}_{\text{NaOH}}}{\sqrt{\overset{\circ}{a}_{\text{H}_2\text{O}}}}$	m'_{OH}	$\log k'_{\text{B}}$	$\log \gamma_{\text{B}}$
0.0	.....	....	......	(−4.2550)	0.0
.1	0.09759	$\bar{1}.7532$	0.002320	−4.2590	+ .0020
.2059	.08145	$\bar{1}.6940$	.002420	−4.2216	− .0167
.3241	.07216	$\bar{1}.6610$	.002382	−4.2357	− .0097
.4837	.06299	$\bar{1}.6306$	.002446	−4.2124	− .0213
.6163	.05786	$\bar{1}.6136$	.002437	−4.2155	− .0198
.7465	.05234	$\bar{1}.5892$	.002639	−4.1456	− .0547
1.0755	.04445	$\bar{1}.5830$	.002526	−4.1841	− .0355
1.5647	.03379	$\bar{1}.5742$	.002683	−4.1310	− .0620
1.7750	.03058	$\bar{1}.5740$	.002681	−4.1316	− .0617
2.1573	.02327	$\bar{1}.5754$	.002923	−4.0555	− .0998
2.7311	.01591	$\bar{1}.5796$	.003045	−4.0194	− .1178

$$\log k_B^\circ - \log k_B' = 2B_B\mu \tag{11}$$

and its intercept corresponds to $k_B^\circ = 5.56 \times 10^{-5}$. To calculate γ_B, the real basic activity coefficient of glycine, we cannot employ Equation 7 directly, because we know neither K_B or k_B. We have, however, demonstrated in our previous paper that $\log k_B'/k_B$ extrapolated to zero ionic

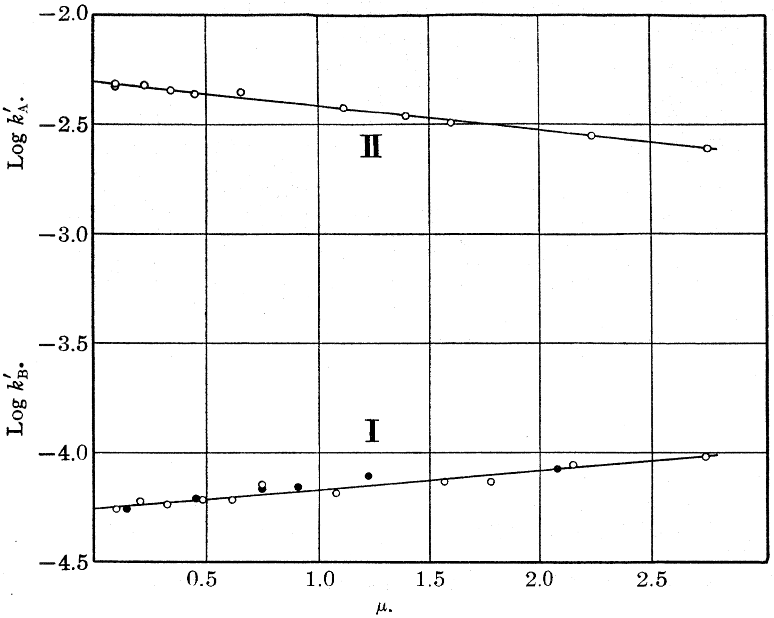

Fig. 1.—Apparent dissociation constants. I, basic; II, acidic

strength becomes $\log k_B^\circ/K_B$, if we are justified in applying to a base this relation discovered for acids. We must also make use again of the hypothesis that this relationship is valid over a considerable range of ionic strengths, so that we may write

$$\log \frac{k_B'}{k_B} = \log \frac{k_B^\circ}{K_B} \tag{12}$$

By combining this with Equation 7, we obtain

$$2 \log \gamma_B = \log k_B^\circ - \log k_B' \tag{13}$$

by which the values given in Table I were calculated. Substituting Equation 11 in 13, we deduce the important relation

$$\log \gamma_B = B_B\mu \tag{14}$$

illustrated by Fig. 2 (I). Indeed this linear variation of $\log \gamma_B$ with μ is to be expected from the nature of γ_B, for, by definition

$$2 \log \gamma_B = \log \gamma_{Z^\pm} + \log \frac{\gamma_{OH^-}}{\gamma_{G^-}} - \log a_{H_2O} \tag{15}$$

Since $Z^{\pm}$ is neutral, the logarithm of its activity coefficient will vary linearly with the salt concentration in dilute or moderately dilute solutions. This is also to be expected for a ratio of ionic activity coefficients of ions of the same valence type. Furthermore, the linear variation of $\log a_{\mathrm{H_2O}}$ will be a close approximation. Hence

$$\left.\begin{aligned} \log \gamma_{Z^{\pm}} &= B_{Z}\,\mu \\ \log \frac{\gamma_{\mathrm{OH}^-}}{\gamma_{\mathrm{G}^-}} &= (B_{\mathrm{OH}} - B_{\mathrm{G}})\mu \\ \log a_{\mathrm{H_2O}} &= B_{\mathrm{H_2O}}\,\mu \end{aligned}\right\} \tag{16}$$

and consequently (14) follows immediately from (15) and (16) by writing $2B_{\mathrm{B}} = B_{Z} + B_{\mathrm{OH}} - B_{\mathrm{G}} - B_{\mathrm{H_2O}}$. These considerations obviously account for the simple linear extrapolation of $\log k'_{\mathrm{B}}$ through Equation **13.**

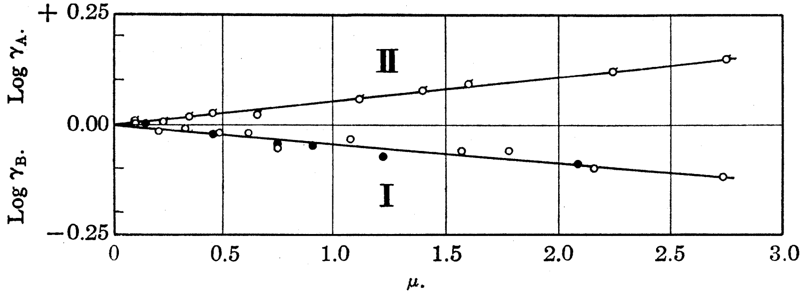

Fig. 2.—Activity coefficient of **glycine.** I, basic; **II,** acidic.

As an important check on the method just outlined, cells in which the silver–silver chloride electrode replaces the amalgam electrode have been employed, and found to give the same numerical results.[11] Since the use of silver–silver chloride single cells in place of amalgam double cells represents a considerable simplification of technique, and a great saving of time, we shall outline the method of calculating our results. It is realized, of course, that the general applicability of the method is limited by the fact that a large number of organic bases have a considerable solvent action upon silver chloride.

If the electromotive force of the reference cell

$$\mathrm{H_2/HCl(0.01)/AgCl/Ag};\ +0.4644 \tag{II}$$

be subtracted from that of the cell

$$\mathrm{H_2/NaG(0.1),\ NaCl(}m\mathrm{)/AgCl/Ag,\ or\ } + \mathrm{E} \tag{III}$$

we obtain the electromotive force, E − 0.4644, of a concentration cell without liquid junction. Thus

$$\mathrm{H_2/NaG(0.1),\ NaCl(}m\mathrm{)/AgCl/Ag/AgCl/HCl(0.01)/H_2} \tag{IV}$$

The equation relating E to the concentrations and activity coefficients is

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[11] Suggested by work recently conducted in this Laboratory by Dr. E. J. Roberts, [THIS JOURNAL, 52, 3877 (1930)].

$$E - 0.4644 = 0.05915 \log \frac{(0.904)^2\,(0.01)^2}{(\gamma_{HCl})^2\, m_H m} \qquad (17)$$

if the activity coefficient of 0.01 molal hydrochloric acid is taken to be 0.904, as given by Randall and Young.[12] m_H Is the hydrogen-ion concentration in the sodium glycinate solution. This equation permits the calculation of m_H, but since m_{OH} is desired, we must introduce the equilibrium expression for the dissociation of water

$$K_w = \frac{\gamma_{H^+}\,\gamma_{OH^-}}{a_{H_2O}}\, m_H m_{OH} = \gamma_w^2 m_H m_{OH} \qquad (18)$$

Giving K_w the numerical value[13] 1.005 X 10^{-14} and combining (17) and (18), we obtain

$$16.9062\,E - 17.7614 + 2\log\gamma_{HCl} - 2\log\gamma_w + \log m = -\log m_{OH} \qquad (19)$$

Just as in the derivation of Equation (10′), we must introduce known activity coefficients in sodium chloride solutions, in the place of unknown activity coefficients in sodium chloride solutions containing sodium glycinate also. In so doing, we define an apparent hydroxyl-ion concentration, m'_{OH}, thus

$$16.9062\,E - 17.7614 + 2\log\overset{\circ}{\gamma}_H - 2\log\overset{\circ}{\gamma}_w + \log m = -\log m'_{OH} \qquad (19')$$

Table II contains the results of the measurements with silver-silver chloride electrodes. The average electromotive force, E, was measured (Cell III) over a period of at least four hours during which the maximum deviation from the mean did not exceed 0.05 millivolt. The values of log $\overset{\circ}{\gamma}_{HCl}$ were read from a plot of the data of Harned,[8] and the values of log $\overset{\circ}{\gamma}_w$ were obtained from a similar plot of $\overset{\circ}{\gamma}_{HCl}$ and $\overset{\circ}{\gamma}_{NaOH}/\sqrt{\overset{\circ}{a}_w}$, and more recent values of $\overset{\circ}{\gamma}_{NaCl}$ determined by Harned.[14] Column 5 contains the values of m'_{OH} computed by Equation 19'. The values of log k'_B and log γ_B were computed as in the preceding section, and are included in Figs. 1 and 2 as inked-in circles. It is obvious that the same straight

TABLE II

THE THERMODYNAMIC PROPERTIES OF SODIUM GLYCINATE SOLUTION BY THE SECOND METHOD

0.1 Molal Sodium Glycinate, m Molal Sodium Chloride; Silver Chloride Electrodes

$\mu = 0.1 + m$	E	2 Log $\overset{\circ}{\gamma}_w$	2 Log $\overset{\circ}{\gamma}_{HCl}$	m'_{OH}	Log k'_B	Log γ_B
0.1470	0.97173	$\bar{1}.7422$	1.7700	0.002326	−4.2566	+0.0008
.4659	.92023	$\bar{1}.6980$	1.7286	.002456	−4.2088	− .0231
.7459	.90620	$\bar{1}.7002$	$\bar{1}.7426$	.002579	−4.1657	− .0447
.9049	.90058	$\bar{1}.7120$	$\bar{1}.7584$	.002607	−4.1563	− .0494
1.2223	.89290	$\bar{1}.7378$	$\bar{1}.7938$	.002755	−4.1075	− .0738
2.0875	.87760	$\bar{1}.8314$	$\bar{1}.9144$	.002863	−4.0738	− .0906

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[12] Randall and Young, THIS JOURNAL, 50,989 (1928).

[13] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances,"McGraw-Hill Book Co., New York, 1923, p. 486.

[14] Harned, THIS JOURNAL, 51,416 (1929).

lines will serve to represent both the plain and inked-in circles within the experimental error.

The Determination of the Dissociation Constant and Activity Coefficient of Glycine as Acid.—The type of cell used to evaluate the acid constants of glycine is identical to that used previously in the study of acetic[15] and formic[4] acids, and to Cell III of this research. Thus E, the measured electromotive force, applies to the cell

$$H_2/HZCl(0.1),\ NaCl(m)/AgCl/Ag;\quad E \qquad (V)$$

from which we subtract, as before, the electromotive force of Cell II to obtain the electromotive force of the complete concentration cell without liquid junction, *viz.*

$$H_2/HZCl(0.1),\ NaCl(m)/AgCl/Ag/AgCl/HCl(0.01)/H_2 \qquad (VI)$$

The equilibrium expression for this cell is

$$E - 0.4644 = 0.05915 \log \frac{(0.904)^2\ (0.01)^2}{(\gamma_{HCl})^2(m + 0.1)m_H} \qquad (20)$$

in which the significance of the symbols and numerical values is obvious from the discussion of Cell III. In simplifying this equation we shall simultaneously replace γ_{HCl} by the known function $\overset{\circ}{\gamma}_{HCl}$ and solve for the apparent hydrogen-ion concentration, thus

$$16.9062\,E - 3.7636 + 2 \log \overset{\circ}{\gamma}_{HCl} + \log \mu = -\log m'_H \qquad (20')$$

The experimental values of E are the averages of the readings taken on each cell over a period of at least four hours in which the maximum deviation from the mean was not over 0.08 millivolt. The values of log $\overset{\circ}{\gamma}_{HCl}$ were read from the same plot used for this purpose in Equation 19′, and are shown in Table III along with E, and m'_H calculated therefrom with the

TABLE III

THE THERMODYNAMIC PROPERTIES OF GLYCINE HYDROCHLORIDE IN SODIUM CHLORIDE SOLUTIONS

0.1 Molal Glycine Hydrochloride, m Molal Sodium Chloride; Silver Chloride Electrodes

$\mu = 0.1 + m$	E	2 Log $\overset{\circ}{\gamma}_{HCl}$	m_H	Lop k'_A	Log γ_A
0.0	.....	....	.....	(−2.3080)	0.0
.1	0.39531	$\bar{1}.7915$	0.01945	−2.3283	.0101
.1	.39495	$\bar{1}.7915$	.01972	−2.3146	.0033
.2278	.37644	$\bar{1}.7492$	.01962	−2.3198	.0059
.3436	.36746	$\bar{1}.7342$	.01910	−2.3460	.0190
.4525	.36110	$\bar{1}.7288$	.01881	−2.3607	.0263
.6546	.35101	$\bar{1}.7354$	.01897	−2.3527	.0224
1.1155	.33643	$\bar{1}.7816$	,01765	−2.4221	.0570
1.3961	.32980	$\bar{1}.8146$	.01692	−2.4627	.0774
1.5997	.32504	$\bar{1}.8408$	.01635	−2.4953	.0936
2.2424	.31254	$\bar{1}.9408$	,01542	−2.5509	.1215
2.7468	.30371	0.0292	.01449	−2.6100	.1510

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[15] Harned and Robinson, THIS JOURNAL, 50,3158 (1928).

aid of Equation 20'. The values of log k'_A given in the fifth column were calculated by the relation log $k'_A = 2 \log m'_H - \log (0.1 - m'_H)$, and are plotted in Fig. 1 (II). As in the case of the basic system, log k'_A is a linear function of μ, and the equation of the straight line is

$$\log k^{\circ}_A - \log k'_A = 2B_A\mu \tag{21}$$

From similar concentrations to those by which we derived Equation 13, we may obtain the expression

$$2 \log \gamma_A = \log k^{\circ}_A - \log k'_A \tag{22}$$

by which the values of log γ_A shown in Table III were calculated. Combination of Equations 21 and 22 leads to the important relation

$$\log \gamma_A = B_A\mu \tag{23}$$

This linear variation of log γ_A with μ is demonstrated experimentally in Fig. 2 (11), and follows theoretically from the definition of γ_A. Thus, for

$$\log \gamma_A = \log \gamma_{Z\pm} + \log \frac{\gamma_{H^+}}{\gamma_{ZH^+}} \tag{24}$$

we may write

$$\log \gamma_A = B_Z\mu + (B_H - B_{ZH})\mu = B_A\mu \tag{25}$$

because the logarithm of the activity coefficient of a neutral particle and the ratio of two ionic activity coefficients of the same valence type are both linear functions of the ionic strength. The extrapolated value of log k'_A at infinite dilution of electrolyte is log k°_A, and is given in Table III in parentheses. This corresponds to the value 4.92×10^{-3} for k°_A.

Summary

1. Making use of 0.1 molal sodium glycinate and glycine hydrochloride solutions, the apparent dissociation constants of glycine have been measured at 25°. The values obtained are $k^{\circ}_A = 4.92 \times 10^{-3}$ and $k^{\circ}_B = 5.56 \times 10^{-5}$. For purposes of comparison, we may write $k^{\circ}_A = K_A$, and $k^{\circ}_B = K_B$, because, for the dilution we have used, the error introduced by this approximation is negligible compared to the discordance among the various values of K_A and K_B recorded in the literature. Branch and Miyamoto[16] list the results of six independent electrometric studies of glycine besides their own. If we include our results and those of Bjerrum and Unmack,[17] the mean values for the nine determinations are $K_A = 4.26 \times 10^{-3}$ and $K_B = 5.14 \times 10^{-5}$, with average deviations from the means of 10 and 13.6%, respectively. This unsatisfactory agreement in the literature can be traced, in no small part, to uncertainties inherent in the methods used. Among these, liquid junctions and unrecognized medium effects are sources of error that are eliminated in the method we have just described. The elimination of liquid junction has actually been carried out

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[16] Branch and Miyamoto, THIS JOURNAL, 52, 863 (1930); cf. Kirk and Schmidt, *U. of California Pub. Physiol.*, 7, 57 (1929).

[17] Bjerrum and Unmack, *Det. Kgl. Danske Videnskab, Selskab, Math.-fys. Medd.*, 9, 1 (1929).

in this paper, but the complicated and laborious study of the medium effect of glycine has just been begun experimentally.

2. It has been demonstrated that the use of silver-silver chloride electrodes or amalgam electrodes leads to identical results in the measurements with alkaline glycine solutions.

3. In the absence of any information concerning the medium effect of glycine, we have drawn, by analogy, upon our study of this subject with acetic and formic acids, and have calculated the activity coefficients of the 0.1 molal amphanion and amphcation in sodium chloride solutions. The logarithms of the activity coefficients are linear functions of the ionic strength, which is in accord with theory.

4. By an exact thermodynamic method which eliminates the use of liquid junctions and which takes into account certain medium effects heretofore neglected, we have shown that the acid and base constants of an ampholyte may be evaluated. Further, in the case of glycine, the first steps toward an experimental solution have been made, and preliminary values of the important constants determined.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION PROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A MANOMETER FOR THE MEASUREMENT OF SMALL PRESSURE DIFFERENTIALS AT HIGH PRESSURES[1]

BY JAMES H. BOYD, JR.[2]

RECEIVED JULY 12, 1930 PUBLISHED DECEMBER 18, 1930

Introduction

In an investigation of the viscosity of compressed gases by the author a new instrument was developed[3] for the measurement of the small pressure differentials which existed between the two ends of a capillary tube through which flowed compressed gas. It relies on electrical means for determining the pressure differential but requires no calibration and does not demand the use of clean mercury to gain accurate results. This manometer is primarily a laboratory precision instrument though by suitable calibration it may be used as a high pressure flowmeter.

The only other instrument for this use at high pressures described in the literature and known to the author is that used by Wildhagen.[4] It

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[1] This article is based on a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Science from the Massachusetts Institute of Technology.

[2] Formerly Research Assistant, Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology. Present address, 3144 Passyunk Ave., Philadelphia, Pa.

[3] J. H. Boyd, Jr., *Phys.* Rev., 35, 1284 (1930).

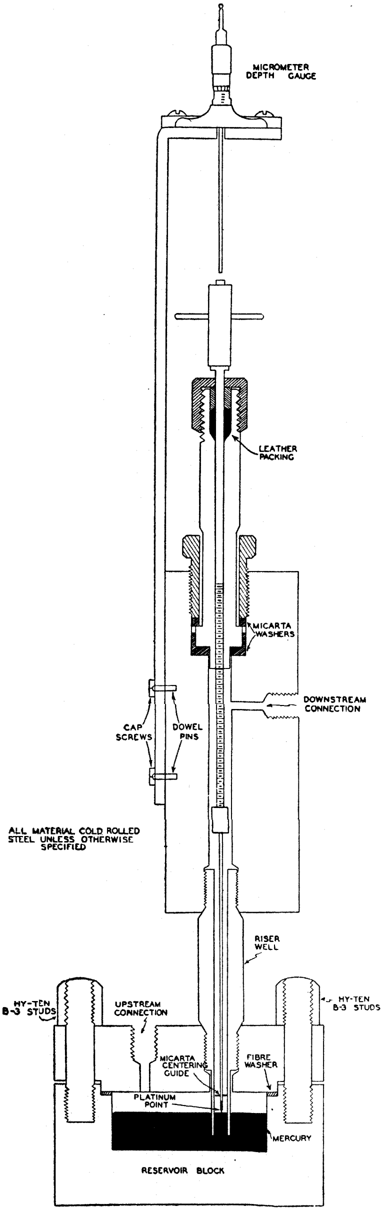
[4] Wildhagen, *Z. angew. Math. Mech.*, 3, 181 (1923).

consisted in principle of a mercury-filled differential steel manometer in one arm of which was a fine platinum resistance wire coaxial with the tube. On applying a pressure differential to the manometer the mercury rose in the arm containing the wire and decreased the electrical resistance of a circuit of which the previously calibrated platinum wire formed the major resistance. In such an instrument errors due to the contamination of the mercury might well prove serious and such fouling is difficult to avoid in practice. Were the mercury contaminated it would adhere to the wire on receding after making an observation and subsequent lesser differential readings would be in error owing to the change in the apparent resistance of the exposed wire.

The New Manometer.—The new differential manometer does not require any calibration and the use of clean mercury is not imperative though ordinary precautions taken to avoid undue contamination are desirable. Essentially, the instrument consists of a mercury reservoir of relatively large diameter (8.9 cm.) beneath whose mercury surface projects the lower end of a riser well of relatively small bore (8 mm.) in which runs a movable screw rod enabling the completion of an electrical circuit through the mercury. The whole is suitably enclosed to permit the use of high pressures. The level of the mercury in the riser well is determined by trial by moving the contact or screw rod so as to make and then break the circuit as indicated by a galvanometer. When this has been done the relative position of the screw rod is determined by measuring the distance to the top of the rod from a fixed reference plane by means of a micrometer depth gage. The difference of such readings when the upstream and downstream pressures are equal and when they are unequal, as is the case for gas flow, is the observed pressure differential. The true differential is obtained on correcting for the drop in level in the reservoir corresponding to the elevation in the riser well, for the buoyant effect of the displaced gas and for the temperature variation of the mercury density. If desired further corrections for the capillarity and compressibility of the mercury may be applied. Calculation showed that pressures up to **3000** lbs. per sq. in. and fluctuations in the room temperature did not affect appreciably the instrument readings.

The construction of the manometer is shown diagrammatically in Fig. 1, which is approximately to scale. A set screw in one of the guide blocks and a stop pin not shown in the drawing allow locking the depth gage in a fixed position. The instrument was designed to give a factor of safety of five based on the ultimate tensile strength of the steel for a working pressure of **5000** lb. per sq. in. at room temperature. The maximum pressure actually used was **3000** lb. per sq. in.

Four auxiliary valves are necessary in the operation of the instrument. Two valves, one in each connection line, permit isolation of the manometer from the rest of the system. A third valve in a by-pass line allows equalization of pressures in the instrument, while the fourth serves as a pressure relief for the mercury reservoir. In addition a mercury trap in the downstream connecting line between the valve and the manometer is desirable to prevent accidental flooding of the rest of the apparatus with mercury.



1.—Diagrammatic sketch of high pressure manometer.

Operation of the Manometer.—The operation of the instrument is quite simple. It is brought under pressure with only the downstream valve open to allow gas to flow down the riser well and under the mercury seal, thus substantially equalizing the pressure in the system. Complete equalization of pressure results on opening the by-pass valve. The zero reading is now made by running the screw rod down until electrical contact with the mercury is made, as shown by the deflection of the galvanometer needle, and then slowly screwing the rod upward until the circuit is just broken. The relative position of the top of the rod on breaking the circuit is determined by measurement with the depth gage from the reference plane. The micrometer gage reads directly to 0.025 mm. (0.001 in.) but the graduations on the barrel permit estimation to 0.0025 mm. (0.0001 in.). The mean of several such readings agreeing within 0.025 mm. (0.001 in.) is taken as the zero reading. This procedure gives very reproducible results. The source of e. m. f. for the circuit is a copper–constantan thermocouple immersed in ice water. The couple is very satisfactory for this purpose as the feeble current so produced minimizes arcing at the mercury surface. After making the zero readings the rod is run up to a greater height than the mercury level anticipated in the ensuing experiment, the by-pass valve is closed and the upstream valve opened. The mercury now rises to its equilibrium position and the observations are again made. In each case the mercury approaches its equilibrium level from below, which tends to introduce a compensation of errors on taking the difference of the two average readings to obtain the apparent pressure differential. The true differential is obtained on applying the corrections previously mentioned. At the conclusion of a series of experiments the pressure in the flowmeter is relieved in order to avoid forcing mercury over into the trap should a leak develop at the rod packing.

Results

The absolute accuracy of the measurement of the pressure differential is not known but in view of the compensation remarked above the error should never exceed the average deviation observed in making a series of zero readings. In Table I a series of consecutive, average zero readings is given which was made over an eight-day period at gage pressures ranging from zero to 3000 lb. per sq. in.

TABLE I

CONSECUTIVE MEAN ZERO DETERMINATIONS, IN INCHES

2.4249	**2.4247**	**2.4265**	**2.4247**
39	**66**	**71**	**45**
82	**62**	**76**	**57**
74	**60**	**73**	**67**
26	**73**	**45**	**43**
57	**59**	**45**	**44**
43	**61**	**51**	**43**

Grand average	**2.4256**
Maximum deviation	**0.0030**
Average deviation	.0011

The tabulated results show the zero reading to be reproducible and indicate that the error in the measurement of a pressure differential does not exceed 0.025 mm. **(0.001** in.). Such accuracy is sufficient for most purposes.

Conclusion

While the instrument described above was satisfactory, certain changes are recommended for future work. The use of a larger riser well will eliminate capillarity effects and also allow the use of **a** larger screw rod whose greater rigidity will make the micarta centering disk unnecessary. In addition the screw rod assembly should be made in two pieces, the lower or contact rod being threaded into the screw rod proper and secured in place by lock nuts. This would necessitate a larger screw rod, which would facilitate packing the rod. Moreover, the bushing through which the rod handle ran and the pin driven into the bushing might well be eliminated.

The author wishes to acknowledge his appreciation of the financial aid granted him by the Research Laboratory of Applied Chemistry and the Committee on Graduate Courses and Scholarships of the Massachusetts Institute of Technology. He also wishes to thank his friends for their many helpful suggestions.

Summary

A manometer has been developed which is capable of measuring by electrical means pressure differentials of an inch of mercury with an accuracy of one part in 1000 at a pressure of 3000 lb. per sq. in. The instrument is direct reading and requires neither calibration nor the use of very clean mercury.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

THE THERMAL HYDROGEN–OXYGEN COMBINATION. FORMATION OF HYDROGEN PEROXIDE, AND THE INFLUENCE OF SURFACE NATURE[1]

BY ROBERT N. PEASE[2]

RECEIVED JULY 18, 1930 PUBLISHED DECEMBER 18, 1930

Hydrogen peroxide has not before been reported as a product of the slow reaction between hydrogen and oxygen which takes place in the neighborhood of 550° and 1 atm. Indeed Rowe[3] states that none could be detected by the sensitive titanium sulfate test. This paper reports the results of some flow experiments in which easily detectable quantities were obtained. In addition there are reported some data on the effect of the nature of the reaction tube surface on the hydrogen–oxygen reaction.

The experiments were of the flow type. Compressed hydrogen and oxygen were passed through flowmeters and a drying system to *a* cylindrical reaction tube of pyrex glass to the ends of which were sealed 2-mm. capillaries. The off-gas passed through a weighing tube cooled to $-79°$. The reaction tube was contained in an electrically heated furnace the temperature of which was automatically controlled to about $\pm 2°$. Hydrogen peroxide was determined by washing out the weighing tube and titrating the product with 0.02 normal potassium permanganate in sulfuric acid solution.

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[1] This paper contains results obtained in an investigation entitled "Catalytic Methods Applied to Petroleum Hydrocarbons" listed as 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 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] Research Associate, American Petroleum Institute.

[3] Rowe, *Z. physik. Chem.*, **59**, 41 (1907).

The Reaction at Atmospheric Pressure.—The data of Table I refer to experiments in which the reaction tube was approximately 1.7 cm. in diameter and 10 cm. long and had a volume of 20.8 cc. The cleaning of the reaction tube is an important point. In this case the tube was rinsed out twice with hot concd. nitric acid, and then a dozen times with distilled water. The total gas flow was usually 40 cc. per minute at 25° and atmospheric pressure (about 760 mm.). Since the reaction rate is subject to considerable variation, each set of data was bracketed with sets to which it was to be compared. The average of three separate determinations is given in each case. Results are expressed in terms of milligrams of products formed per half-hour, and also as exit-gas concentrations (in 0.01 atm., calculated for 25° and 1 atm. total pressure). In most of the runs the entering gases were saturated with water vapor at 0°, as the behavior of the reaction was somewhat more steady under these conditions. This water was subtracted from the total found in the weighing tube. Complete conversion of 10 cc. per minute of hydrogen in a half hour would yield 220 mg. of water.

TABLE I

WATER AND HYDROGEN PEROXIDE FROM HYDROGEN AND OXYGEN

Temp., °C.	Reactants cc./min.		Formed mg. per half hour		Exit-gas concns. in 0.01 atm.	
	H_2	O_2	H_2O	H_2O_2	H_2O	H_2O_2
			Effect of Drying			
540	30	10				
Dried at		0°	56.8	2.04	6.41	0.13
Dried at		−79°	47.5	1.83	5.38	.11
Dried at		0°	51.1	1.92	5.79	.12
			Effect of Heating Time			
540	10	10	61.0	0.77	13.8	0.09
	30	30	19.3	1.95	1.46	.08
	10	10	67.5	0.90	15.3	.11
			Effect of Composition			
540	10	30	13.0	1.19	1.47	0.07
	30	10	50.3	2.15	5.70	.13
	10	30	6.6	0.92	0.74	.06
			Effect of Temperature			
540	10	30	4.8	0.68	0.54	0.04
550			16.9	1.29	1.91	.08
540			1.3	0.63	0.15	.04
540	30	10	35.3	1.64	4.37	.10
530			16.7	1.08	1.89	.06
540			36.4	1.61	4.12	.10

In spite of the irregularity of the results, certain conclusions as to the formation of water and hydrogen peroxide may be drawn. It is, first of all, clear that the initial presence of traces of water vapor is not essential. When the heating time is cut to one-third by tripling the gas flow, the off-gas concentration of water vapor is cut to one-tenth while that of the peroxide is not measurably altered. The reaction is clearly auto-accelerated so far as water formation is concerned. The peroxide appears to attain an approximate steady-state concentration. One cannot conclude from these data that hydrogen peroxide is the sole primary product but the results point in that direction.

Experiments on the effect of hydrogen-oxygen ratio show clearly that formation of both products is more rapid with excess of hydrogen. Water formation is again the more affected. A rise of 10° in reaction tube temperature increases the yield of water 2- to 4-fold, and about doubles the peroxide formed over the range studied. The temperature coefficient appears to depend on the $H_2:O_2$ ratio.

These results may be taken to indicate that hydrogen peroxide is a primary product of the hydrogen–oxygen reaction, that water is formed auto-catalytically, and that the reaction is favored by a high ratio of hydrogen to oxygen as well as by high temperature.

There are many other conclusions that might be drawn from these and the quantities of other data on the reaction which we have obtained. Aside from the above, however, the only certainty is that the highly capricious behavior of the reaction mixture in pyrex reaction vessels has made this a most unsatisfactory reaction to deal with. According to Hinshelwood,[4] the reaction in silica vessels is very similar in behavior, glazed porcelain being rather more satisfactory to work with.

The Reaction at Low Pressures.—Hinshelwood[5] has reported the extraordinary fact that hydrogen–oxygen mixtures become unstable and explode within a restricted low-pressure range at temperatures above about 450°. It was of interest to confirm this by a somewhat different method and especially to determine whether the formation of hydrogen peroxide could be detected. Accordingly the flow apparatus was altered to include a three-way stopcock before the reaction tube, a reaction tube about 1 cm. in diameter by 10 cm. long into which the reaction gases passed via a drawn-out capillary, and a vacuum pump and gage for reducing and reading the pressure at the outlet end. With these alterations a number of runs were made. Results are recorded in Table II.

The results are essentially in agreement with those of Hinshelwood as to the existence of an upper pressure limit. There was immediate (but not complete) reaction up to a certain pressure and then a rapid decrease in reaction rate at higher pressures. A significant feature of the results is that no trace of hydrogen peroxide was detectable in the region of rapid action. Nevertheless, at higher pressures with only small amounts of

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[4] Gibson and Hinshelwood, *Proc. Roy. Soc.* (London), **119A,** 591 (1928).

[5] Thompson and Hinshelwood, *ibid.*, **122A,** 610 (1929).

TABLE II

HYDROGEN-OXYGEN REACTION AT LOW PRESSURES

Gas rates, 20 cc./min. for each gas (measured at 25° and 1 atm.); reaction tube volume about 7 cc.

Temp., °C.	Press., mm.	Mg. of H_2O per 10 min.	
500	5 to 10	Nil	H_2O_2 less than 0.05 mg.
	25	Nil	
525	5 to 10	42.4	
	25	43.0	
	50	9.0	
	75	Nil	
550	5 to 10	86.8	
	25	83.2	
	50	79.4	
	75	63.4	
	400 (approx.)	1.6	— H_2O_2 = 0.28 mg.

water being formed, hydrogen peroxide was obtained in easily detectable amounts. In this connection it is to be remembered that the exposure time was shorter in proportion at the lower pressures. The failure of hydrogen peroxide to escape from the reaction tube at the low pressures in the explosion region might be ascribed to the high temperatures attained in the gas. It is not unlikely, however, that the peroxide is itself accountable for the explosivity. A possibility is that a freshly-formed peroxide molecule is subject to dissociation yielding atomic oxygen. If the molecule enters into collision with a normal molecule within a minimum time after formation, it is stabilized. Failing this, it dissociates and produces the chain of results characterizing the explosion. High pressures would favor stabilization, while low pressures would permit of dissociation.

Effects Due to Surface.—Hinshelwood[4,5] has shown that the hydrogen–oxygen reaction is repressed when the reaction vessel is packed with broken wall-material, in the case of porcelain and silica vessels. Data showing that this is also true for pyrex reaction vessels are given in Table III. In addition, the importance of the nature of the surface is brought out by data in this table. When either an empty or a packed reaction tube is rinsed out with a potassium chloride solution, the reaction rate is subject to a marked decrease. Thus, whatever the action of the glass surface may be in suppressing reaction, this action is enhanced by coating the glass with a film of potassium chloride. The special feature of this effect is that it is so marked in the empty tube. Although no direct comparison was made, the rate must be reduced about 2000-fold by the coating.

Without detailing the results, it may be said that treatment with potassium hydroxide solution is about equally as effective as treatment with potassium chloride. In addition, treatments with solutions of aluminum nitrate, barium nitrate, arsenious chloride or phosphoric acid were

TABLE III

HYDROGEN–OXYGEN COMBINATION. EFFECT OF PACKING AND COATING

Gases flowing at 20 cc. per minute each. Reaction-space volume, 20.0 ± 0.5 cc.

	Empty tube		Packed tube	
	Cleaned with HNO_3	Rinsed with KCl soln.	Cleaned with HNO_3	Rinsed with KCl soln.
Temp., °C.	Mg. water plus hydrogen peroxide formed per minute			
510	0.02			
520	.07			
530	.22			
540	.63			
550	Explos.		0.13	0.02
575			.65	.03
590		0.06		
600		.19	5.34	.07
610		.58		
625		Explos.	10.4	.43
650				.63

all more or less effective. This is in comparison with the same tube when rinsed first with nitric acid and with water. Treatment with a copper nitrate or chromic acid solution caused a marked increase in rate, due no doubt to positive surface catalysis. Yet even in these cases it is significant that no hydrogen peroxide was formed, and that the kinetics were so altered as to suggest that the original reaction had again been suppressed. It may be mentioned that no treatment gave better yields of hydrogen peroxide than the original one with hot concd. nitric acid.

Summary

1. The hydrogen–oxygen combination in pyrex reaction vessels has been studied by the flow method.
2. It has been found that hydrogen peroxide is formed in readily detectable amounts along with water. The former may be the primary reaction product.
3. The reaction mixture becomes unstable at low pressures and reacts explosively, but yields no peroxide under these conditions.
4. Reaction may be partially suppressed by filling the reaction vessel with broken pyrex glass or better by coating its inner surface with any one of a number of substances, among which is potassium chloride.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

THE SPECIFIC HEATS OF GASES AT HIGH PRESSURES. II. METHOD AND APPARATUS AT HIGH TEMPERATURES[1]

BY NORMAN W. KRASE AND B. H. MACKEY

RECEIVED AUGUST 11, 1930 PUBLISHED DECEMBER 18, 1930

Introduction

This paper is the second of a series from this Laboratory reporting methods and measurements of the specific heats of gases at high pressures and over a range of temperatures. The first paper[2] described the apparatus developed for use at ordinary temperature and over a range of pressures to 1000 atmospheres. The present one describes a new calorimeter suitable for measurements over the entire range of pressures and up to temperatures of 350° or more. The experimental method is essentially the same as previously described, the new features being concerned entirely with the calorimeter and thermostat. The arrangement of gas storage cylinders, compressor and recirculating system is unchanged. In order to carry the measurements to higher temperatures, an entirely new calorimeter and thermostat were designed and built.

The Thermostat and Calorimeter

Reference to Fig. 1 in the first paper in this series[2] shows the function of the thermostat. This piece of apparatus must be capable of delivering gas at the desired pressure and temperature to the calorimeter at a constant rate of flow. For temperatures used in this work a satisfactory thermostat was built by coiling up about 3.5 meters of 6.5-mm. by 1.5-mm. steel tubing and casting a cylindrical block of copper around the coiled portion. An electric heater was wound on the casting and a Beckmann thermometer placed in a hole drilled in the casting. The temperature was manually controlled by external resistances and could be held to about 0.01°. The gas leaving the thermostat entered the calorimeter through a short, well-insulated tube.

The calorimeter is shown in Fig. 1. The gas, preheated to a temperature usually 5 or 6° below the calorimeter temperature, enters through the horizontal tube shown sectionally at the left.

It passes down through the vertical tube, also shown in section, through the coiled portion, then up through the right-hand tube and out through the horizontal tube shown in full. The coiled portion of the calorimeter tubing is embedded in a copper casting 7.5 cm. long and 6.4 cm. in diameter. This casting also contains an electric heater and a thermometer. By means of the heater the temperature of the calorimeter block is maintained constantly about 5 or 6° above the temperature of the thermostat. During its passage, therefore, the gas takes heat from the calorimeter and its temperature rises. The heat taken up by the gas is continuously supplied by the electric heater, so that the temperature of the calorimeter remains constant. To reduce as much as possible the heat losses by conduction, radiation, etc., the calorimeter is enclosed in a pyrex Dewar flask having an internal diameter of 7 cm. and an internal length of 29 cm. Surrounding

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[1] Presented at the Atlanta meeting of the American Chemical Society, April 9, 1930, before the Division of Physical and Inorganic Chemistry.

[2] Krase and Mackey, THIS JOURNAL, 52,108 (1930).

the Dewar flask is a heavy, cylindrical copper casting 46 cm. long, 10 cm. inside diameter, and having a wall 15.5 mm. thick. Copper disks close both ends of the cylinder; openings in the upper disk are provided for the necessary electrical leads, the thermometer, and the two steel tubes carrying thermocouple wires shown in the drawing. The other wires and the thermometer and heater are not shown. In order to operate the calorimeter adiabatically, the copper jacket is kept at the same temperature as the calorimeter by means of an electric resistance heater wound around the casting. A thermometer inserted in a hole drilled through the top disk and into the wall of the cylinder indicates the jacket temperature. A thick layer of insulation covers the jacket.

This calorimeter differs from the one previously described particularly because of certain improvements in the method of measuring the temperature rise of the flowing gas and the heat losses by conduction along the steel tubing.

As will be noted in Fig. 1, the wires comprising the couples for reading the rise in temperature of the flowing gas enter at the top ends of steel tubes extending about 13 cm. above the calorimeter cover. This arrangement not only removes the bakelite compression seals from the heated zone but also reduces the temperature gradient along the portion of the tubes through which the gas flows. This latter fact is extremely important in reducing heat conduction losses along the steel tubing. A secondary advantage, also, is the reduction in heat flow along the thermocouple wires as a result of this arrangement. The ends of the coiled calorimeter tubing are connected by "gradient" tubes having a uniform steel cross section for a length of 10 cm. to the gas inlet and outlet tubes. Five copper–constantan thermocouples equally spaced along each of these gradient tubes provide readings of the temperature drop along the tubes and thus data for calculating the heat

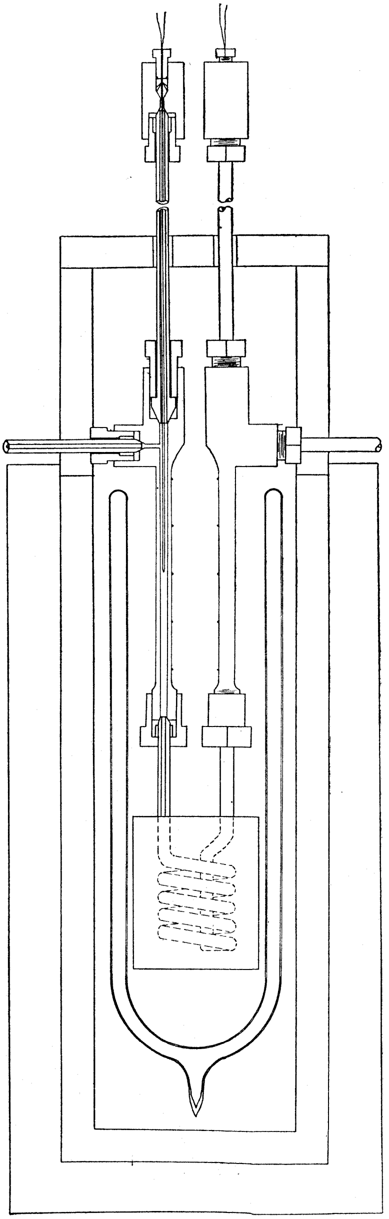

Fig. 1.

flow away from the calorimeter block. The thermojunctions for measuring gas temperature rise are located at the midpoint of the uniform section of the gradient tubes. The thermocouples can be removed from position and calibrated without disturbing the bakelite seals or other connections.

For calorimeter temperatures to 150° Beckmann thermometers are most satisfactory. Since these thermometers are used only to indicate constancy of temperature, the absolute temperature need be known only to about one-tenth of a degree. The settings were checked using liquids of known boiling points as calibration standards.

Experimental Methods

Reference to the first paper is suggested for experimental details. In addition to the measurements described previously it was thought desirable to know the absolute temperature of the gas leaving the calorimeter. The usual experimental routine involved measuring only the gas temperature rise—not its absolute temperature. Since the question of average gas temperature for a given measurement is important for accurate work, a number of experiments were performed designed to measure the exit temperature of the gas. A copper–constantan couple similar to those used in the calorimeter was inserted together with the Beckmann thermometer in the jacket well and the constantan wire connected with that of the couple in the exit tube of the calorimeter. If the exit gas temperature and jacket temperature were the same, the reading of the couples would be zero. The results of a number of such trials showed that the exit gas reached practically the same temperature as the calorimeter within an experimental error of about 0.06". Practically perfect heat transfer was, therefore, accomplished between gas and calorimeter and the temperature of the calorimeter may be taken as the gas temperature for all purposes.

In this work, the rates of gas flow used ranged from 0.7 to 1.5 moles per minute and the results were entirely independent of rate of flow, indicating the absence of systematic errors in measurements. Further refinements in measuring the rate of gas flow involved enclosing the indicating capillary meter and the wet meter as well as the gas humidifier in a compartment whose temperature was thermostatically controlled. Small changes in temperature were sufficient to alter the calibration of the wet meter considerably.

The use of an adiabatic calorimeter at elevated temperatures involves heating the jacket to practically the same temperature as the calorimeter. In the present case this was accomplished by winding a nichrome electrical resistance coil on the copper casting and passing a 110-volt alternating current through it, controlled by an external resistance. It was found that this arrangement generated heat by induction in the copper casting inside the Dewar flask. The effect was very considerably reduced by using a non-inductive winding on the jacket but was not entirely eliminated. Separate measurement of this induced heat was, therefore, necessary at each calorimeter temperature used. The use of direct current for jacket heating was the obvious remedy but this, unfortunately, was not available. The correction was measured by using the same gas flow as during a regular experiment but raising the thermostat temperature so that the gas entered the calorimeter at practically the calorimeter temperature. No heat was supplied to the calorimeter proper except that received by induction from the jacket current. The rise in gas temperature was measured and this subtracted from the observed rise in the regular experiment. The correction measured in this way not only included the induced heat but also any heat change due to a Joule–Thomson effect within the calorimeter.

Table I shows typical results for nitrogen from 30 to 150° at 500 atmospheres pressure. A subsequent paper will give complete data for nitrogen over a range of pressures to 700 atmospheres and temperatures to 150°.

TABLE I

TYPICAL RESULTS FOR NITROGEN

Experiment no.	30	80	108	122
Absolute pressure, atm.	500	500	500	500
Av. calorimeter temp., °C.	30	50	100	150
Gas temp. rise, °C.	6.85	6.84	7.63	6.78
Gas flow, moles/min.	1.412	1.496	1.335	1.383
Heat loss by conduction	0.1	0.15	0.2	0.3
Heat gain by induction	...	0.5	1.4	4.7
Corrected power input	88.2	90.6	85.4	76.5
Molal heat capacity	9.12	8.85	8.39	8.13

Summary

A constant-temperature, adiabatic, flow calorimeter for the measurement of specific heats of gases at high pressures and temperatures has been developed. Typical results for nitrogen together with the methods of measurement and calculation are given.

URBANA, ILLINOIS

[Contribution from the Laboratory of Inorganic Chemistry, Department of Chemistry, University of Wisconsin]

THE STRENGTH OF ORGANIC BASES IN GLACIAL ACETIC ACID SOLUTION[1]

By Norris F. Hall

Received August 26, 1930 Published December 18, 1930

Although the earlier papers of this series have frequently dealt with the titration of organic amines in glacial acetic acid, the subject has been treated more or less incidentally, and only scattering selections have been made from the available data. In the present paper are summarized the results of a study of a large number of these compounds, and it has been possible to draw certain conclusions of interest to the general theory of acidity. A clear parallelism has been found between the strengths of these bases in acetic acid and in water, and the results are compared with similar results by other workers in three other solvents.

Table I presents an alphabetical list of the bases successfully studied, and the numerals used to identify them on the diagrams.

Table I

List of Bases Studied with Identifying Numerals

Acetamide	11	Formanilide	3b
Acetanilide	5	Guanidine	52f
Acetoxime	19	N-Methylacetanilide	8
p-Aminodimethylaniline	52b	Methylaniline	37b
Ammonia	52c	Methylethylaniline	52a
Anisalacetophenone	2	Methyl-*n*-propylaniline	51
m-Anisidine	34	Methyl-o-toluidine	41
o-Anisidine	38	Methyl-*p*-toluidine	42b
p-Anisidine	35	Methylurea	14
Antipyrine	25	α-Naphthylamine	32
Benzylaniline	36a	o-Nitro-aniline	9
m-Bromo-aniline	27	p-Nitro-aniline	18
o-Bromo-aniline	23	3-Nitro-4-chloro-aniline	21a
p-Bromo-aniline	31	4-Nitro-2,6-dichloro-aniline	1b
m-Chloro-aniline	26	m-Nitrodimethylaniline	22
o-Chloro-aniline	24	*p*-Nitrodimethylaniline	12
p-Chloro-aniline	30	*p*-Nitrosodiphenylamine	28
Colchicine	21b	Phenylurea	10
Diacetylmonoxime	3a	α-Picoline	47
Di-n-butylamine	52e	Piperidine	49

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[1] This is the fifth of a series of acidity studies to which the present author has contributed. Earlier papers have appeared under the title "Studies in Superacid Solutions" as follows: Hall and Conant, This Journal, 49, 3047–3061 (1927) (herein referred to as "I"); Conant and Hall, *ibid.*, 49, 3062–3070 (1927) (II); Hall and Werner, *ibid.*, 50,2367–2386 (1928) (III); and Conant and Werner, *ibid.*, 52,4436 (1930) (IV). The principal results of this paper were presented at the Swampscott meeting of the American Chemical Society in September, 1928.

TABLE I (Concluded)

2,4-Dichloro-aniline	20	Propionitrile	1a
2,5-Dichloro-aniline	17	N-Propylacetanilide	7
Diethylamine	50a	Pyridine	45
Diethylaniline	53b	Quinoline	42a
Diethyl-*o*-toluidine	55	Semicarbazide	29
Diethyl-*p*-toluidine	54b	m-Toluidine	33
Dimethylamine	46	o-Toluidine	36b
Dimethylaniline	44	*p*-Toluidine	37a
s-Dimethyldiphenylurea	4	Tribromo-aniline	6
Dimethylpyrone	15	Tri-n-butylamine	52d
Dimethyl-o-toluidine	54a	Triethanolamine	53c
Diphenylamine	16	Triethylamine	54c
Diphenylguanidine	48	Triphenylguanidine	50b
Di-n-propylaniline	53a	Urea	13
Ethylaniline	43		

Method of Study.—The bases were all titrated in 0.05 molar solutions with perchloric acid as has been previously described.[2]

The potentials reported are those of cells of a type already pictured[3] and the former convention has been used to define "$P_{\text{H}}^{(\text{HAc})}$." The temperature was 25 ± 2°. Results are reported in this section of the paper for those bases only whose curves showed no marked abnormality such as is caused by rapid reaction with chloranil, the formation of precipitates, or the formation of hemi-perchlorates.

Experimental Results

If the titration data are all plotted on a single diagram (Fig. 1),[4] the assemblage of curves has a considerable resemblance, in spite of differences noted below, to such theoretical plots of the curves of unequally strong acids or bases in water as, for example, the one given by Britton.[5]

Survey of the Titration Curves.—For convenience in discussion, the bases are divisible into three groups. The first group comprises the weakest bases, as far down as No. 11 (acetamide) and includes those whose curves show no appreciable break. The second or intermediate group extends from *p*-nitrodimethylaniline (12) to #-bromo-aniline (31) and includes bases whose curves show both an initial rise and a break at the end of the titration. The remaining (strongest) base curves show no initial rise. The points of division between the groups are of course somewhat arbitrary.

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[2] (III) Hall and Werner. THIS JOURNAL, 50,2367–2386 (1928).

[3] Hall and Werner, *ibid.*, p. 2369 and Fig. 3.

[4] The drawing of the unnumbered curves near the bottom of Fig. 1 is somewhat schematic.

[5] H. T. S. Britton, "Hydrogen Ions," D. Van Nostrand Co., New York, 1929, p. 127, Fig. 36.

Bases of Intermediate Strength.—In the second or intermediate group the curves all run substantially parallel throughout most of their course, as required by the elementary theory of titration, but their e.m.f.

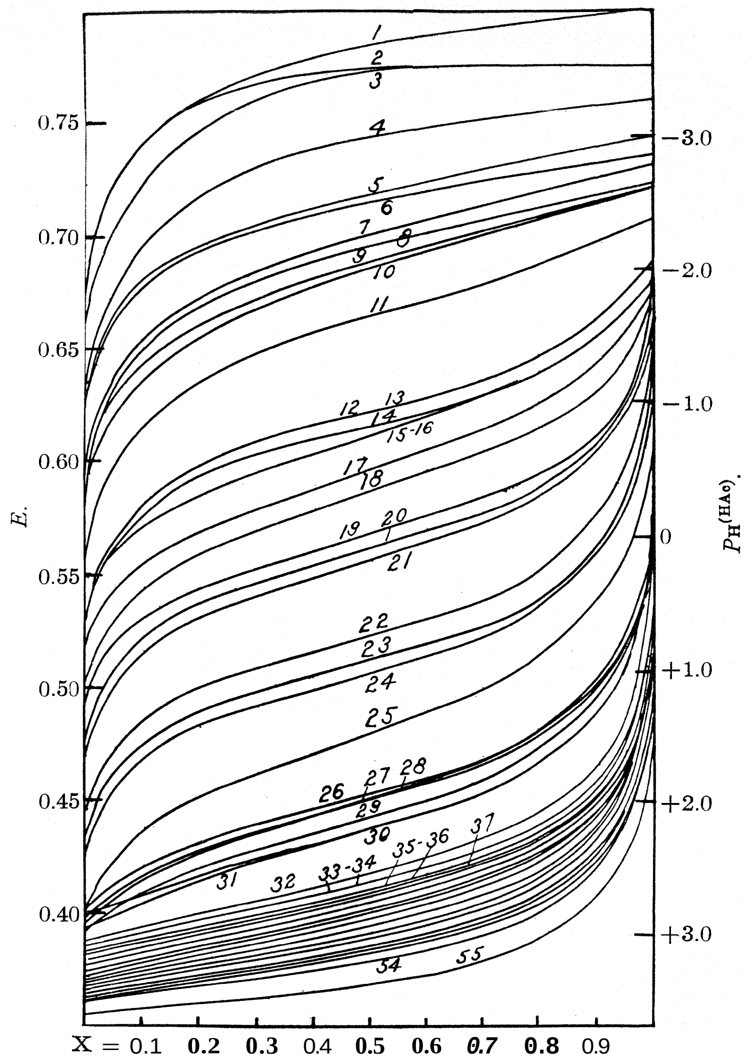

Fig. 1.—Titration curves of 0.05 M bases in glacial acetic acid.

values, as pointed out by Hall and Werner (III), are not even approximately a simple function of log R, (R = $x/(1 - x)$ (x = fraction titrated)), so that the curves appear "too flat" when compared with similar curves obtained in water. It is reasonable to ascribe this anomaly to the change in activity coefficients caused by the increase in ionic strength during titration, and evidence on this point has already been presented by Conant and Werner (IV).

In an attempt to formulate quantitatively the voltage changes during titration, the voltages at round values of x were read from a large plot of Fig. 1 for the middle group of bases. These voltages were converted into $P\text{H}^{(\text{HAc})}$ values by the formula $(0.566-E)/0.0591 = P\text{H}^{(\text{HAc})}$. To these observed $P\text{H}^{(\text{HAc})}$ values were added the values of log R for each point and the resulting \$K^{t} values plotted against $x^{1/2}$. It then appeared that in every case pK' was nearly a linear function of $x^{1/2}$.

As examples, the values of pK' for the first three bases of the group are given in Table II, together with the corresponding values of a + bx''. The average deviation of the two sets of values is also shown.

TABLE II

pK' AS A FUNCTION OF x

p-Nitrodimethylaniline

x	= 0.10	−0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
pK' (obs.)	= −1.29	−1.17	−1.09	−1.00	−0.92	−0.87	−0.83	−0.76	−0.64
$-1.58 + 0.917x^{1/2}$	= −1.29	−1.17	−1.08	−1.00	−0.93	−0.87	−0.81	−0.76	−0.71

Average deviation, ±0.01

Urea

x	= 0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
pK'	= −1.22	−1.12	−1.06	−0.99	−0.91	−0.87	−0.83	−0.76	−0.64
$-1.48 + 0.816x^{1/2}$	= −1.23	−1.13	−1.04	−0.97	−0.91	−0.86	−0.82	−0.76	−0.72

Average deviation, ±0.02

Methylurea

x	= 0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
pK'	= −1.15	−1.04	−0.98	−0.91	−0.82	−0.77	−0.70	−0.65	−0.52
$-1.45 + 0.896x^{1/2}$	= −1.17	−1.05	−0.96	−0.88	−0.82	−0.76	−0.70	−0.65	−0.60

Average deviation, ±0.02

The formulas used for these three bases are fairly representative of all the others in this group—(with the exception of antipyrine, which shows a much steeper curve)—and it seems desirable in order to save space, not to report the results in full. The constants a and b are mutually adjustable within narrow limits and their theoretical significance is obscure. If pK' is plotted against $\mu^{1/2}$ instead of $x^{1/2}$ the points approximate slightly less closely to a straight line (μ is the concentration of the added acid. μ and x are not strictly proportional because of the appreciable volume of the titrant, nor is the relation between the two always the same because of the use of titrants of more than one concentration). Certain systematic trends in the deviations of the experimental points seem to indicate that functions of $x^{1/2}$ of the type stated are only first approximations to the values of pK'. The reproducibility of the data is insufficient at present to warrant the use of a more complicated approximation formula. Instead of $pK' = a + \text{b}\, x^{1/2}$ or $pK' = a + b'\mu^{1/2}$, it is conceivable that in this concentration range curves of the form $pK' = a'' + b''\mu^{1/2} - \text{b}''cr\mu$ as required by a form of the Debye–Hückel theory might fit the data. If the dielectric constant of pure acetic acid at 25° is 6.17 as obtained by interpolation in the data of Smyth and Rogers,[6] b" should have the value $23.0 and c should be $+1.17$. The constant $10^{-8}r$ is the so-called ion radius and should be positive. Equations of this form with these constants do not fit the data. It is probable that due to the presence of water (up to 0.5%) the dielectric constant of the solvent was higher than 6.17, possibly even as high as 10. And it is further possible that it changed during titration under these conditions, so that a theoretical approach along these lines seems unpromising.

The Strongest Bases.—When a weak base is dissolved in acetic acid it may be assumed that the reaction of salt formation $B + HAc \rightleftharpoons BH^+Ac^-$ is very incomplete, while with a strong base it is virtually complete. When a weak base is titrated the reaction $B + HClO_4$ $BH^+ClO_4^-$ (or $B + H^+(HAc)$ $BH^+ + HAc$) removes the free base and alters the concentration ratio of the cation to the free base remaining with resulting changes in the proton activity since

$$p_{H^{(HAc)}} = pK'^{(HAc)} - \log \frac{a_{BH^+}}{a_B}$$

A strong base is already completely converted into salt when the titration starts, and the only effect of the titration is to substitute a perchlorate for an acetate. The increase in proton activity will depend directly on the removal of acetate since $a_{H^+} \times a_{Ac^-} = \text{const.}$ In this latter case the ionic strength does not change during the titration, and the activity coefficients of the ions remain constant as shown by Hall and Werner's analysis of titration curves of the "strong base" type (III).

Between these two extreme cases, in acetic acid as in water, there exists a group of "transition" bases in which both the free base and its acetate may be assumed to exist together in the solution in appreciable quantities at the start of the titration. These should give curves of intermediate form, and such curves are readily observed in Fig. 1. The lowest curve in the diagram (diethyl-o-toluidine) is clearly anomalous for unknown reasons; dimethyl-o-toluidine (54a) and diethyl-*p*-toluidine (54b) show similar anomalies but to a less extent, and smaller variations are observed for other bases, above and below the "typical" or "average" strong base curve.

The Weakest Bases.—As the base strength diminishes, the tendency to react with even so strong an acid as perchloric acid becomes less and finally disappears, so that a point is finally reached where a solution of the base behaves toward the addition of perchloric acid as though the solvent alone were present (Curve 1, bases 1a, 1b). Bases of progressively diminishing strength give curves which should be the transposed mirror images of the transition and strong base curves at the bottom of the diagram. Because of the relative unreliability of the measurements in this highly acid

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[6] Smyth and Rogers, THIS JOURNAL, 52, 1824–1830 (1930).

region, it has not been very thoroughly studied and secondary influences evidently distort some of the curves obtained.

Comparison with the Water System.—The basicity constant of a

$$K_{\text{Bas.}} = \frac{1}{a_{\text{H}^+}} \times \frac{c\text{BH}^+}{c\text{B}}$$

given base dissolved in a protogenic[7] solvent HX depends only on the intrinsic strength of the base and on the activity coefficients f_{BH^+} and f_{B}. These latter are primarily influenced by the acidity and basicity constants and the dielectric constant of the solvent, but also exhibit individual variations. If these are not too great, it should be possible to establish a pairwise correspondence between the basicity constants of a series of bases in any non-aqueous solvent and in water. In sufficiently dilute solution in

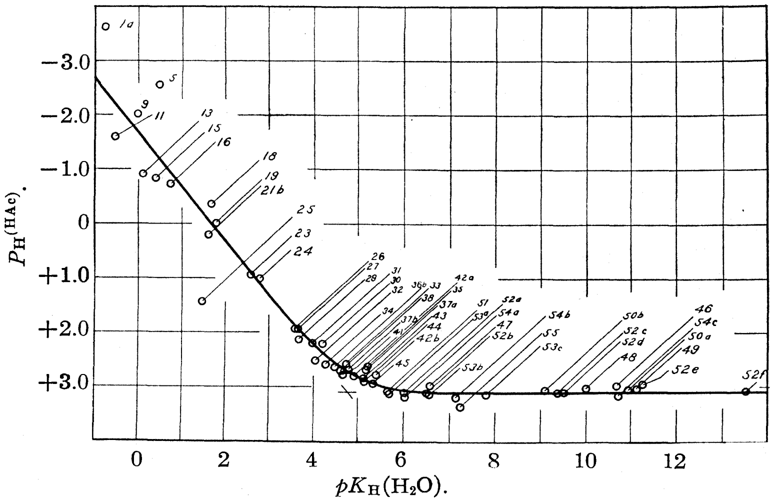

Fig. 2.—Comparative strength of bases in acetic acid and in water.

water $K_{\text{Bas.}}$ for any base is simply the reciprocal of the ordinary hydrolysis constant (*i. e.*, $K_{\text{Bas.}} = K_{\text{B}}/K_{\text{W}}$). In another solvent $\log K_{\text{Bas.}} = P_H + \log R$. In acetic acid $K_{\text{Bas.}}$ is far from constant when the concentration or the value of R is varied, so that it is necessary to choose a particular concentration and value of R, as well as to keep the titrating acid the same in comparing different bases. No satisfactory extrapolation of the values of $K_{\text{Bas.}}$ to infinite dilution has been possible here. The values to be compared with pK_{H} in water are therefore those of $\log K_{\text{Bas.}}^{(\text{HAc})} = P_{\text{H}}^{(\text{HAc})} + \log R$ at $R = 1$, *i. e.*, at the midpoint of titration. This has been done for 52 bases in Fig. **2** for which the necessary data are given in Table V. The abscissa is $\log K_{\text{Bas.}}^{(\text{H}_2\text{O})} = pK_{\text{H}} = \log K_{\text{B}} + pK_{\text{W}}$. The ordinate is the value of $P_{\text{H}}^{(\text{HAc})}$ at the half titration point $= pK'^{(\text{HAc})} = \log K_{\text{Bas.}}^{(\text{HAc})}$

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[7] Brönsted, *Z. angew. Chem.*, 43, 229–233 (1930).

for each base as read from Fig. 1. The line on the diagram needs further explanation.

If bases at a given concentration in water are titrated with a strong acid, the P_H of the titration midpoints increases with the strength of the base so that it is almost exactly 9 for $pK_B = 5$, 10 for $pK_B = 4$, etc., etc. However, as pK_B diminishes, a point is reached, depending on the concentration of the solution, where the increase in P_H at the midpoint is no longer proportional to the decrease in pK_B. The P_H values now approach a certain maximum which is that shown by a completely ionized base half-titrated under the conditions of the experiment. Thus if the total base is 1 N, the P_H at the midpoint of titration should be 13.7 (neglecting activity coefficients). All bases with K_B above a certain value will show midpoint P_H's experimentally indistinguishable from **13.7.** What this limiting value will be depends on the concentration and the precision of measurement. It is clear that in the case of these strongest bases, the equilibrium

$$B + H_2O \rightleftharpoons BH^+, OH^-$$

is effectively completely displaced to the right even before the titration starts. It is also clear that any solvent capable of releasing a proton to the molecule B should behave in this respect just like water.

$$B + H\,Sol \rightleftharpoons BH^+, \bar{S}ol$$

but that the value of $K_{Bas.}$ at which the maximum P_H is reached should differ with each solvent.

It follows from this discussion that if P_H (midpoint) in any protogenic solvent is plotted against pK_H for a series of bases, the points will lie on a line of slope $= -1$ over a considerable range. At a certain point, depending on the concentration, this line will begin to bend upward and change with an easily calculable curvature into a horizontal line passing through the limiting P_H for the concentration in question. Such a line is the one drawn for acetic acid in Fig. *2*. In this figure the line is drawn as follows: (a) the slope of the left-hand portion is fixed at -1. (b) The curvature of the middle part is determined from the simple theory outlined above. (c) The ordinate of the horizontal part is fixed by the average ordinate of the experimental points for the strongest bases. (d) The three parts of the curve thus restricted are then fitted together so as best to reproduce the experimental points. This semi-empirical method of placing the curve evidently results in a satisfactory fit. One may conclude from Fig. *2* that there is a very definite parallelism between the strengths of the bases in the two solvents but that individual minor departures from exact parallelism are the rule rather than the exception. Both of these conclusions are in accord with previous knowledge of acid strength in solvents other than water.

It must not be forgotten, moreover, that the water values used are averaged from the results of numerous investigators, working at different times and places and by different methods. Under such conditions it is rather surprising that the scattering of the individual points is no greater than it is. Among the very weak bases, measurements are reproducible with difficulty both in water and in acetic acid, so that a greater than normal scattering is there to be expected. (The one unmistakable and significant exception is that of antipyrine (25). This base exhibits no unusual titration behavior in water, but in acetic acid it has a titration curve much steeper than any of the others. It seems possible that this irregularity is due to a reaction with chloranil or to a molecular rearrangement of the base.)

It is interesting to note the value of pK_{H} at which the bases become "strong" in acetic acid. If the two straight portions of the curve are extended, they intersect at a point which has an abscissa $pK_{\mathrm{H}} = 4.75$ (approx.). This is almost exactly the figure representing the strength of acetate ion as a base in water. In other words, it appears from these results that the relative base strength of molecules such as those of the chloroanilines, pyridine, etc., and of the acetate ion remains the same when these substances are transferred from water to acetic acid.

In view of the substantial regularities disclosed by Fig. 2, it is reasonably safe to use it in predicting the strength in water of bases for which no measurements are available. Table III lists those bases which have been successfully titrated in acetic acid but whose constants in water are unknown to me. With each base is given its serial number, its midpoint $pK'^{(\mathrm{HAc})}$ value and its predicted pK_{H} value in water.

TABLE III

DATA FOR BASES

No.	Name	$pK'^{(\mathrm{HAc})}$ obs.	$pK_{\mathrm{H}}^{(\mathrm{H_2O})}$ predicted
1b	4-Nitro-2,6-dichloro-aniline	−3.69	<−1
2	Anisalacetophenone	−3.50	<−1
3a	Diacetylmonoxime	−3.49	<−1
3b	Formanilide	−3.49	<−1
4	s-Dimethyldiphenylurea	−3.00	<−1
6	Tribromo-aniline	−2.52	−0.8
7	N-Propylacetanilide	−2.27	− .6
8	N-Methylacetanilide	−2.17	− .5
10	Phenylurea	−2.01	− .3
12	*p*-Nitrodimethylaniline	−0.92	4 .8
14	Methylurea	− .82	+ .9
17	2,5-Dichloro-aniline	− .51	+1.2
20	2,4-Dichloro-aniline	+ .08	+1.8
21a	3-Nitro-4-chloro-aniline	+ .19	+1.9
22	m-Nitrodimethylaniline	+ .73	+2.4
28	*p*-Nitrodiphenylamine	+1.93	+3.5

Moreover, in the case of certain bases, even though precipitation or other disturbing effects were noted, it is possible from an inspection of the titration curve to predict roughly what the strength in water should be. This has been done for a few additional bases in Table IV.

TABLE IV

PREDICTED STRENGTH OF CERTAIN BASES IN WATER

	pK_H
Acetylphenylhydrazine	$+1.3$
p-Amino-acetophenone	$+2.75$
Benzamide	-1
Carbazole	<-1
Dimethylglyoxime	<-1
p-Nitrosodiethylaniline	$>+5.5$
Pyrrole	$+0.4$

From a few titrations with sulfuric acid one may infer that dianisylcarbinol has a $pK_H < -1$ and hydrobenzamide $> +5.5$.

The following bases, the constants of many of which are at least approximately known in water, could not be titrated satisfactorily in acetic acid under the conditions used for the reason indicated.

Base Insufficiently Soluble.—Alloxantine, dipiperonalacetone, dianisalacetone, tyrosine.

Precipitation Occurred.—Acetone semicarbazone, o-aminobenzoic acid, *p*-aminobenzoic acid, 4-aminodiphenyl, asparagine, benzidine, diphenylanisylcarbinol, dipiperonalacetone, ethylenediamine, glycocoll, hexamethylenetetramine, Michler's ketone, β-naphthylamine, m-nitro-aniline, α-nitroguanidine, β-nitroguanidine, *p*-nitrosodimethylaniline, xanthydrol.

Base Apparently Formed a **Hemi-perchlorate.**—Aminoazobenzene, diazo-amidobenzene, dimethylaminoazobenzene.

Base Reacted with **Chloranil.**—Aniline, hydrazine hydrate, methylphenylnitrosamine, p-nitrophenylhydrazine, phenylhydrazine, piperine, taurine, thiourea.

Titration Curve Had an Irregular Form.—p-Phenylenediamine, *o*-phenylenediamine, quinaldine, thiocarbanilide.

Data Used in Preparing Fig. 2.—In Table V are given in order the identifying numeral of the base, its name, the $P_H^{(HAc)}$ of the titration midpoint as read from a large plot of Fig. 1, the preferred value of pK_H for the base in water at 25° as determined by averaging the values in the next column, the particular values selected from the literature and used in computing the average, and a letter or letters indicating the literature reference from which the value in question was obtained. Figure 2 was drawn with the values in Columns 3 and 4 of Table V as ordinate and abscissa, respectively.

TABLE V

STRENGTH OF BASES IN ACETIC ACID AND IN WATER

		$pK'^{(HAc)}$	$pK_H^{(H_2O)}$		
1a	Propionitrile	−3 65	−0 80	−0.8 W. L.	
5	Acetanilide	−2 59	+ 4	+0.3 Wo.	+0.5 Re.
9	*o*-Nitro-aniline	− 203	+ 06	+ .06 Lo.	+ .06 G. I
11	Acetamide	− 164	− 48	− .45 W. L.	− .50 E. O.
13	Urea	− 093	+ .10	+ .10 W. W. L.	+ .13 Z.
				+ .05 Ko.	
15	Dimethylpyrone	− .76	+ .40	+ **.30** Wald.	.49 Spr.
16	Diphenylamine	− .74	+ .85	+ .64 Far.	+1.06 Thi.
18	p-Nitro-aniline	− .36	+1.9	2.03 Lo.	1.8 Re.
19	Acetoxime	− .05	+1.75	1.77 Lun.	1.75 Wo.
				1.74 W. L.	
21b	Colchicine	+ .19	+1.65	1.65 Ko_2	
23	o-Bromo-aniline	+ .90	+2.60	2 60 G.	
24	o-Chloro-aniline	+1.00	+2.77	2.77 G.	
25	Antipyrine	+1.45	+1.51	1.66 Ko_1	1.46 Spr.
				1.49 B. G.	1.5 Osb.
				1.42 Re.	
26	m-Chloro-aniline	+1.93	+3.52	3.47 Fliir.	3.56 G. K.
27	m-Bromo-aniline	+1.93	+3.51	3.51 Fliir.	
29	Semicarbazide	+2.13	+3.66	3.67 Wo.	3.65 Spr.
30	p-Chloro-aniline	+2.20	+4.00	4.07 F. W.	3.93 Fliir.
31	*p*-Bromo-aniline	+2.20	+3.91	3.94 F. W.	3.87 Fliir.
32	α-Naphthylamine	+2.54	+3.99	3.92 F. W.	4.04 Spr.
				4.02 H.	
33	*m*-Toluidine	+2.57	+4.71	4.78 Miz.	4.74 Br. D
				4.67 Fliir.	4.70 Spr.
				4.67 Bred.	
34	*m*-Anisidine	+2.59	+4.21	4.21 Spr.	
35	*p*-Anisidine	2.62	5.30	5.30 Spr.	
36b	*o*-Toluidine	2.65	4.43	4.45 Miz.	4.47 Br. D.
				4.41 Bred.	4.40 Spr.
37a	*p*-Toluidine	2.67	5.12	5.09 D. S.	5.08 Spr.
				5.20 Br.	5.12 Pring
				5.10 Fliir	5.13 H.
				5.20 Lo.	5.07 Br. D.
37b	Methylanilinc	2 67	4.78	4.79 Miz.	4.86 Spr.
				4.70 Pring	
38	*o*-Anisidine	2.69	4.51	4.51 Spr.	
41	Methyl-o-toluidine	2.77	4.60	4.60 Spr.	
42a	Quinoline	2.79	4.87	4.92 Bred.	4.81 H. K.
				4.90 G. S.	4.83 B. G. S.
42b	Methyl-p-toluidine	2.79	5.34	5.34 Spr.	
43	Ethylaniline	2.83	5.14	5.15 Pring	5.13 Spr.
44	Dimethylaniline	2.86	5.10	5.17 B. G. K.	5.10 L. G.
				5.03 Miz.	5.06 Spr.
				5.12 Pring	
45	Pyridine	2.93	5.21	5.05 Miz.	5.26 G. S.
				5.29 Lu.	5.24 B. G. S.
				5.21 H. K.	

TABLE V (Concluded)

		$pK'^{(HAc)}$	$pK_H^{(H_2O)}$		
46	Dimethylamine	2.96	10.71	10.69 Miz. 10.70 I. C. T.	10.73 H. S. 10.70 Br. S.
47	α-Picoline	2.98	6.5	6.65 G. S.	6.43 C. W.
48	Diphenylguanidine	3.01	10.0	10.0 Kr. 10.0 H.	10.0 Spr.
49	Piperidine	3.03	11.09	11.10 Bred	11.08 H. S
50a	Diethylamine	3.05	10.95	11.00 Bred.	10.90 Spr.
50b	Triphenylguanidine	3.05	9.1	8.9 Kr.	9.3 Bar.
51	Methyl-*n*-propylaniline	3.08	5.62	5.62 Spr.	
52a	Methylethylaniline	3.10	5.99	5.99 Spr.	
52b	*p*-Aminodimethylaniline	3.11	6.48	6.59 H.	6.37 Mc.C.
52c	Ammonia	3.10	9.27	9.32 Lund. 9.31 N. K. S.	9.25 Miz.
52d	Tri-*n*-butylamine	3.10	9.85	9.85 Spr.	
52e	Di-n-butylamine	3.10	11.18	11.18 Spr.	
52f	Guanidine	3.10	13.5	13.5 Spr.	
53a	Di-n-propylaniline	3.13	5.60	5.60 Spr.	
53b	Diethylaniline	3.15	6.52	6.64 Pring 6.55 Spr.	6.36 L. G.
53c	Triethanolamine	3.15	7.78	7.78 Spr.	
54a	Dimethyl-o-toluidine	3.20	5.92	5.87 Spr.	5.96 L. G.
54b	Diethyl-*p*-toluidine	3.20	7.09	7.09 Spr.	7.09 Spr.
54c	Triethylamine	3.18	10.74	10.72 Br.	10.75 H.
55	Diethyl-o-toluidine	3.36	7.16	7.16 Spr.	

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NOTES ON TABLE V

It was necessary to make a complete resurvey of the literature in preparing Table V. In this the well-known compilation of Scudder[8] was of great assistance as were the various large tables of physico-chemical data. All these sources must be used with caution for the following reason. Although most determinations of base strength in water are made by a hydrolytic method which leads directly to the calculation of K_{H} instead of K_{B}, the data are all converted to values of K_{B} in the tables *with the use of a great variety of values for* K_{w}, so that it is nearly always necessary to go to the original paper in order to find out which value of K_{w} was used in the particular computation under review. The advantages of the pK_{H} values used in this paper over the values of K_{B} are obvious. Moreover, as the bases must be compared at a single temperature (here 25°), many of the data in the literature which apply to some other neighboring temperature are useless unless a suitable temperature correction can be applied to them. Mr. Sprinkle in this Laboratory has determined the temperature coefficient of pK_{H} for a number of bases of different strengths, and found the coefficient to increase with the base strength from about $\Delta pK_{\mathrm{H}}/\Delta t = 0.01$ at $pK_{\mathrm{H}} = 4$ to about $\Delta pK_{\mathrm{H}}/\Delta t = 0.02$ at $pK_{\mathrm{H}} = 11$. This work will shortly be published in connection with new determinations of the strength of a variety of bases in water. The coefficients found by Mr. Sprinkle have been used in correcting to 25° those data in the literature which were obtained at temperatures from 15 to 40°, where a determination on a given base at 25" by the same author was lacking.

The values cited do not represent a complete list of the values published up to the present time. The determinations of Veley, aside from being made at low temperatures and by unreliable colorimetric methods, are so discordant with other work as to appear valueless and have not been included. They may be found in Scudder, and in Landolt-Bornstein. The work of Bourgeaud and Dondelinger,[9] while in many cases it agrees with that of others, has been justly criticized by various authors[10] as fundamentally unreliable, and includes a number of values so fantastically incorrect as to make it seem advisable not to include any of it in the averages. The values of Farmer and Warth have also

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[8] Scudder, "The Conductivity and Ionization Constants of Organic Compounds," D. Van Nostrand Co., New York, 1914.

[9] Bourgeaud and Dondelinger, Bull. *soc. chim.*, 43, 37, 277 (1925).

[10] See, for example, Carothers, THIS JOURNAL, 49,2908–2914 (1927).

been criticized by Flürscheim and are mostly distinctly too low (*i. e.*, pK_H is too low). They have been omitted except in a few cases.

The work of Myrback is peculiar in that every one of his values of pK_H is lower than the most probable value by an amount varying from 0.07 to 0.51 P_H units (average 0.25). The use of a string soaked in concentrated hydrochloric acid as a salt bridge from his saturated calomel electrode to the weakly acid solution he was measuring, as well as a temperature drop of 7° along his salt bridge, may have contributed to these discrepancies His reasons for preferring his own results are not convincing, and I have used them only when other reliable values were lacking.

During the correction of the proof it was found that certain data of Kuhn and Wassermann[10a] had been overlooked in preparing Table V and Fig. 2. The additional values are: for 9, o-nitro-aniline, -0.3, making $pK_H(H_2O) = -0.06$; for 18, p-nitro-aniline, $+1.0$, making $pK_H(H_2O) = +1.6$. The effect of both of these changes would be to bring the corresponding points in Fig. 2 closer to the line, and this would be true to a still greater extent if the values of Farmer and Warth for these bases (-0.32 and $+1.02$) were also included. The revised values would then be -0.13 and -1.4.

Acid Strength in Other Non-aqueous Solvents.—Results somewhat similar to those in the present paper have been reported by other authors for other solvents as follows. Michaelis and Mizutani[11] and Mizutani[12] have shown that in various methanol–water and ethanol–water mixtures the acidity constants of numerous uncharged acids on the one hand and cation acids on the other exhibit roughly equal changes within each class for a given change in composition of the solvent. Goldschmidt and Mathiesen[13] by aminolytic measurements have shown much the same thing in regard to dissociation constants of the two types of acids in absolute methanol, absolute ethanol and certain aqueous mixtures. Brönsted,[14] by a colorimetric method, has determined the relative acidity constants of numerous indicators and uncolored acids in benzene. Acids of the same type are evidently nearly equally affected by transfer from water to benzene, while the strength of cation acids is relatively greatly increased by this transfer.

Materials.—Practically all the bases studied were purchased from the Eastman Kodak Company. A few were obtained from laboratory stock at the Harvard Chemical Laboratory and in this Laboratory and these were specially prepared or purified before use. In most, but not all, cases the Eastman liquids were redistilled and characterized by their boiling points, and the melting points of the solids were determined. Where necessary, special purification processes were used. I am indebted to Professor Tenney L. Davis for certain urea derivatives, and to Dr. Wallace H. Carothers for a number of amines and amides. The other materials were prepared and used as described in the earlier papers.

[10a] Kuhn and Wassermann, *Helv. Chim. Acta*, **11**, 3 (1928).

[11] Michaelis and Mizutani, *Z. physik. Chem.*, **116**, 135–159 (1925).

[12] Mizutani, *ibid.*, **118**, 318–326; 327–341 (1925).

[13] Goldschmidt and Mathiesen, *ibid.*, **119**, 439–473 (1926).

[14] Brönsted, *Ber.*, **61**, 2049–2063 (1928).

Acknowledgment.—I should like to express my thanks to Messrs. Tyrrell H. Werner, Marshall R. Sprinkle and Victor A. Reinders for assistance in making many of the measurements and for the communication of certain data (to be published later) on the strength of bases in water.

It is further a great pleasure to acknowledge the aid received from a grant from the Milton Fund of Harvard University covering the purchase of many of the bases studied.

Summary

1. A large number of organic bases have been titrated with perchloric acid in glacial acetic acid solution.

2. It is shown that the relative strengths of the bases in acetic acid and in water are nearly proportional and that. it is possible to determine by titration in acetic acid the "water" strength of certain bases which cannot be studied in water.

3. A large part of the published data on the strength of bases in water has been critically resurveyed and the values "corrected" to 25° where necessary in accordance with new determinations of the temperature coefficient of pK_H for bases of different strengths.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE AGRICULTURAL COLLEGE]

A STUDY OF THE DENSITY, SURFACE TENSION AND ADSORPTION IN THE WATER–AMMONIA SYSTEM AT 20°[1]

BY H. H. KING, J. LOWE HALL AND GLEN C. WARE

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In view of the fact that liquid ammonia behaves as an ionizing medium for electrolytes it was thought that the determination of its behavior as a polar liquid toward adsorbed substances containing polar groups would be of interest. As a preliminary step this investigation is concerned with the surface tension of water–ammonia mixtures as compared with the theoretical values for ideal mixtures obtained by Whatmough's rule.[2] The resemblance of these two liquids as a solvent can be thus quite satisfactorily indicated. Incidentally some indication of the extent to which ammonia is associated in the liquid state may be observed.

Surface tension in liquid ammonia has been investigated by Berthoud[3] but the range of his work was not extensive. Rice[4] recently has made

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[1] Contribution No. 155, Department of Chemistry.

[2] W. H. Whatmough, *Z. physik. Chem.*, **39**, 129 (1901).

[3] A. Berthoud, *Helv. Chim. Acta*, **1**, 84 (1918).

[4] O. K. Rice, *J. Phys. Chem.*, **32**, 584 (1928).

determinations upon solutions up to a concentration of 14 moles per liter. Apparently Rice's method lacked certain refinements, particularly precautions relating to distillation from the capillary surface, thorough mixing and density determinations.

It was necessary to develop a method for determining the density of solutions, for no data upon the density of ammonia–water mixtures at 20° could be found in the literature for concentrations above 50% ammonia.

Experimental Procedure

The capillary height method was used to determine the surface tension. The apparatus, a modification of the Richards and Coombs type, was constructed of a heavy grade pyrex tubing (Fig. **1-A**). The cylindrical bowl, *35* mm. in diameter, was used to provide a surface of such size that its center portion would provide a flat surface. A capillary side arm was attached to the bowl below and to the stem above with a gooseneck at its juncture with the stem. This design permitted thorough irrigation of the capillary at will and yet prevented the liquid which drained down from the walls after agitation of the contents from draining into the capillary.

The bowl was banded by three rings etched into the glass. These served only as a guide when filling the tube so that the quantity of liquid introduced could be approximated quickly and controlled. The portion of the tube above the juncture of the side-arm to the stem was designed to serve as a pycnometer. The barrel and the small tube attached were of such size that the volume of the pycnometer measured from the upper end down to the upper end of the graduated scale in the stem was about equal to the volume of the bowl and side-arm up to the middle ring of the bowl. This provided an apparatus easily handled in which the density and surface tension of a given solution could be determined without the necessity of transferring it to other apparatus or even unsealing the tube. Errors in transference of solutions or escape of gaseous substances were entirely eliminated.

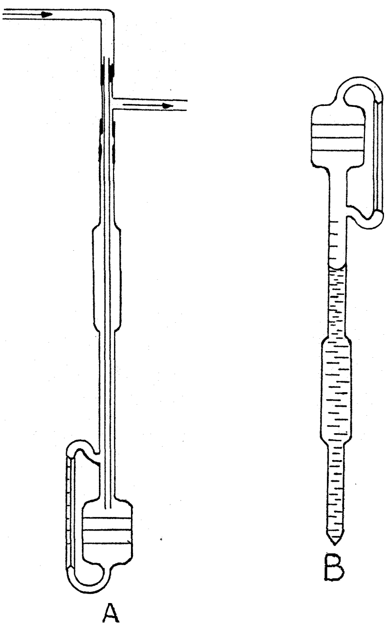

Fig. **1**.—**A**, Showing method of introducing ammonia vapor into apparatus where it is condensed; B, showing method of measuring volume of vapor phase in density determination. The total volume is determined subsequently.

Gaseous ammonia was condensed into the tube by carbon dioxide snow. Figure **1** shows how the apparatus was connected to fill the tube. The gas was led first to a drying train consisting of freshly ignited aluminum oxide. **A** T-tube with rubber connections through which protruded a small bore tube which reached down into the top part of the bowl was used to introduce the gas into the tube.

Last in the train of apparatus was a mercury trap which served to control and increase pressure and condensation. The tubes were dried, weighed and then filled with sulfuric acid-dichromate cleaning solution and allowed to stand until the next fill.

They were then thoroughly rinsed with surface tension water and dried only when to be filled with pure ammonia.

When sufficient ammonia was condensed, the delivery tube was partly removed from the apparatus until the rim of the tube was softened in the flame; then the delivery tube was held just above the opening until the apparatus was sealed. In this manner air was excluded while the tube was being sealed. In measurements where density determinations were to be made, the tip, or sealed-off piece, was retained to be included in further weighings. Capillary height readings were taken with a William Gaertner calibrated traveling microscope.

Densities for solutions above 50% ammonia at 20° were determined by weighing the tube before and after filling and measuring the volume of the pycnometer on the calibrated volume scale, the tube being in the inverted position shown in Fig. 1-B while volume readings were taken. The water sample was weighed in, ammonia was introduced, and the tube was sealed off and weighed. After reading the capillary height the tube was inverted and the volume of the vapor was read on the calibrated scale on the stem of the pycnometer. The volume of the liquid was determined by difference after the total volume of the tube had been measured. The tube was opened by heating at the tip with a needle flame after the pressure had been greatly reduced in carbon dioxide snow. When the tubes were opened a small pin-hole was blown through the tip The sharp edges were melted back, and the minute bulb raised with the pin-hole was shrunk back to its former shape. Thus the volume of the tube was not altered,

Meniscus volume corrections were made by means of the Bashforth and Adams data in the "International Critical Tables," Vol. I, p. 73. Corrections for air buoyancy were made on all weighings.

Obviously the vapor, especially at high pressures, would contain enough ammonia to affect the calculated value of the density. The tables of Wilson[5] were used to give the total vapor pressure of ammonia–water mixtures and the composition of the vapor phase corresponding to each solution composition studied. The density of the vapor present was assumed to be directly proportional to the pressure and the mean molecular weight of the vapor.

$$D = D_a \cdot \frac{P}{P_a} \cdot \frac{M}{M_a}$$

in which D_a, P_a and M_a refer, respectively, to the density, pressure and molecular weight of the vapor above pure ammonia and D, P and M refer, respectively, to the density, pressure and mean molecular weight of the vapor above the solution. Since the vapor over the solutions whose densities were determined in no case contained greater than a few tenths of 1% of water vapor, no objectionable error was introduced by omitting the second proportionality factor from density calculations. The density of saturated ammonia vapor at 20° was taken as 0.007474 from the Landolt–Börnstein Tables. However, in the data for pure liquid ammonia the vapor and liquid densities were taken from the Bureau of Standards Circular No. 142, Tables of Thermodynamic Properties of Ammonia.

Sufficient density determinations were made to determine the curve

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[5] T. A. Wilson, *Univ. Illinois, Eng. Exptl. Sta. Bull.* No. **146 (1925).**

plotted in Fig. 2. These were plotted on sufficiently large scale to be read to the fourth significant figure.

Apparatus.—All pieces of apparatus were carefully calibrated. The diameters of the capillaries were carefully determined by measuring the length of a weighed pellet of mercury at successive positions in the capillary. An additional check was made with the purest obtainable thiophene-free benzene.

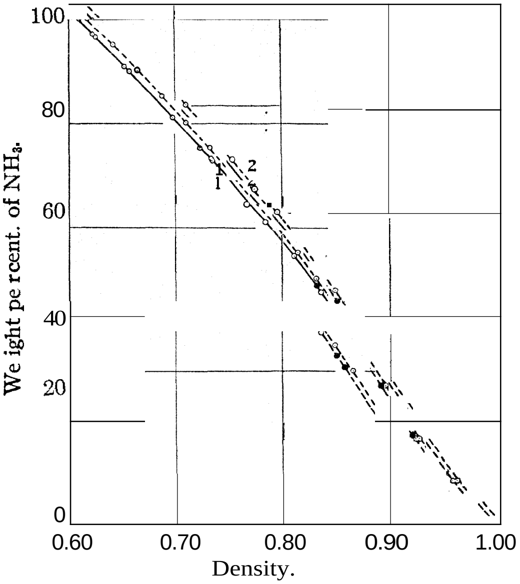

Fig. 2.—1, Densities of water–ammonia mixtures at 20°. Solid line covers range of experimental determinations. Solid circles are determinations by Mittasch, Kuss and Schlueter. Lower points from "International Critical Tables." 2, Densities at 15° for comparison taken from "International Critical Tables."

The formula used for calculating surface tension was

$$\gamma = \frac{r\,(h + r/3)\,(d - D)g}{2}$$

in which r is the radius of the capillary, h the capillary height, d the density of the liquid, and D the density of the vapor.

Discussion of Results

The surface tension of liquid ammonia as determined in this work agrees closely with Berthoud's[3] value at 11.1° if his data are calculated by the corrected capillary height formula as given above. Measurements at 0° were made in a transparent Dewar tube.

In the range of 0–20° the molecular weight of liquid ammonia was calculated by the differential method of Ramsay and Shields.[6] The value of K was found to be 1.662, indicating an apparent molecular weight of 24.5, or approximately 3/2 NH_3. Such a condition must indicate an equilibrium mixture of two or more molecular components, as possibly $(NH_3)_2$ (60%) $\rightleftarrows$ $2NH_3$ (40%). The surface tension–temperature data in Table II when plotted appear to lie in a nearly straight line, indicating a temperature coefficient of 0.220 dyne per degree centigrade.

The determined densities of solutions above 50% NH_3 are tabulated in Table I and plotted in Fig. 2 along with data from Mittasch, Kuss and Schlueter,[7] and with data from the "International Critical Tables."

[6] Ramsay and Shields, *Z. physik. Chem.*, 12,431 (1893).

[7] Von A. Mittasch, E. Kuss, and H. Schlueter, *Z. anorg. allgem. Chem.*, **159**, 1 (1926).

TABLE I

EXPERIMENTAL DATA FOR SURFACE TENSION OF WATER–AMMONIA MIXTURES (TEMP., 20 ± 0.01°)

Wt. % NH_3	Rad. of cap., cm.	Density of soln.	Cap. ht. (corr.), cm.	Surf. tens., dynes/cm.	Moles/liter NH_3	Ammonia adsorption moles/sq. cm. X 10^{11}
100.00	....	0.61029	....	22.03	35.836	0.000
97.36	0.03344	.6232	2.2600	22.81	35.628	0.000
97.18	.03477	.6240[a]	2.1681	22.78	35.608	....
96.68	.03477	.6262[a]	2.1895	23.09	35.550	
96.66	.03334	.6263[a]	2.2764	23.02	35.548	....
91.41	.03344	.6505	2.3426	24.70	34.917	....
90.94	,03450	.6530	2.2359	24.42	34.870	
90.81	.03470	.6531[a]	2.3261	24.57	34.826	
89.81	.03335	.6577[a]	2.3604	25.11	34.682	0.000
89.72	.03335	.6585	2.3681	25.22	34.693	....
80.95	.03472	.6984[a]	2.3876	28.11	33.198	0.000
78.38	.03335	.7094	2.5530	29.34	32.651	
75.07	.03464	.7240[a]	2.5061	30.57	31.915	
72.49	.03335	.7356[a]	2.6700	31.84	31.312	....
72.56	.03466	.7354[a]	2.5381	31.44	31.334	+32.013
70.47	.03336	.7443	2.7325	32.99	30.799	+29.271
64.51	.03472	.7705[a]	2.7539	35.87	29.187	+18.879
63.64	.03340	.7744	2.8938	36.40	28.940	+18.879
61.16	.03468	.7850[a]	2.8574	37.90	28.192	+18.879
54.40	.03468	.8111[a]	3.0335	41.63	25.909	....
53.48	.03340	.8149	3.2114	42.65	25.591	+11.491
47.45	.03346	.8363[a]	3.3965	46.42	23.302	....
44.56	.03339	.8458	3.4831	48.08	22.132	− 3.283
35.98	.03347	.8730	3.6559	52.29	18.444	− 3.283
29.70	,03349	.8890	3.8136	55.58	15.504	− 5.746
24.14	.03347	.9094	3.8948	58.02	12.891	− 5.746
14.61	.03349	,9409	4.0304	62.15	8.072	− 7.387
7.72	.03350	.9661	4.1507	65.74	4.378	− 3.283
0.45	.03349	.9960	4.4444	72.55	0.264	+ 9.850

[a] Densities determined. Other densities taken from curve.

TABLE II

TEMPERATURE COEFFICIENT OF SURFACE TENSION OF PURE AMMONIA

Temp., °C.	Radius of cap., cm.	Cap. ht., cm.	$d - D$	Surface tension
0.0	0.03609	23,554	0.63511	26.44
0.0	.03625	23.423	.63511	26.42
0.5	.03458	24.501	.63433	26.33
10.0	.03609	22.181	.61985	24.31
10.0	.03625	22.029	.61985	24.25
20.0[a]	....	....	.60360	22.03

[a] Average of twelve determinations ranging from 21.94 to 22.09.

The data from all three sources agree very well. The density curve at 15° was included in broken lines for the purpose of comparison. The solid line portion of the lower curve in Fig. 2 represents the values determined experimentally. The accuracy is indicated from the fact that the density curve joins closely with the points obtained by Mittasch, Kuss and Schlueter[7] and that the curve follows closely the character of the 15° density curve. The eight density determinations on pure ammonia, averaging 0.61026 (range 0.6100–0.6107) compared with the Bureau of Standards value of 0.61029, is additional evidence to show the accuracy and dependability of the method used in this work.

The surface tension values found in Table I were calculated from experimental data, the densities being taken from the curve. All surface tension determinations were made under conditions such that the percentage composition of the solution could be determined even though the volume were not such as to make a density determination possible.

Rice[4] has made surface tension determinations of solutions of ammonia in water up to a concentration of 14.08 moles per liter. His values throughout were lower than those obtained in this work with a greater difference at lower concentrations. Since Rice determined density by transferring solutions to a pycnometer and reading the concentration from density–concentration tables, disagreement of results is to be expected. Rice ascribed fluctuations in capillary height to the action of ammonia on glass; they could equally as well be ascribed to a state of unequilibrium because of difficulty in obtaining thorough mixing in the system, also to the fact that the apparatus was not enclosed in a thermostat.

The pyrex glass apparatus used in this work gave no cause for any suspicion as to its reaction with ammonia. When the system had been given time to come to temperature equilibrium, the contents had been thoroughly mixed, and the capillary had been irrigated several times, the capillary height became constant within a moderate period of time necessary for the draining of the walls of the apparatus.

The observed surface tension values were compared with theoretical values obtained by Whatmough's[2] modification of the Volkmann rule

$$\gamma = (V_1\gamma_1 + V_2\gamma_2)R$$

in which V_1 and V_2 are the volume fractions of the components, γ_1 and γ_2 are the surface tensions of the pure components, and R is the ratio of the calculated to the observed density. The values are shown graphically in Fig. 3. It is to be observed that the theoretical and observed surface tensions are in good agreement except in the middle region, where a divergence of less than six dynes occurs. It is of interest to note that the vapor pressure of the system goes through a marked depression from the normal in this region, thereby conforming to Worley's rule[8] of perfectly miscible liquids. Worley shows for a number of mixtures that abnormalities of surface tension tend to move contrariwise to abnormalities in vapor pressure.

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[8] Worley, *J. Chem. Soc.*, 105, 273 (1914).

It is evident from the surface tension and thermodynamic standpoint that the system does not deviate radically from what is to be expected of a perfect mixture. No doubt the formation of ammonium hydroxide contributes to such deviation, but no attempt is made to take it into account. Consequently it is to be expected that liquid ammonia would behave as a polar liquid similar to water, and that orientation of substances on the surface of liquid ammonia would be quite similar to their orientation on water surfaces. The surface tensions of solutions of ammonium salts of aliphatic acids in liquid ammonia are being investigated at present in this Laboratory with the intention of determining the surface adsorption.

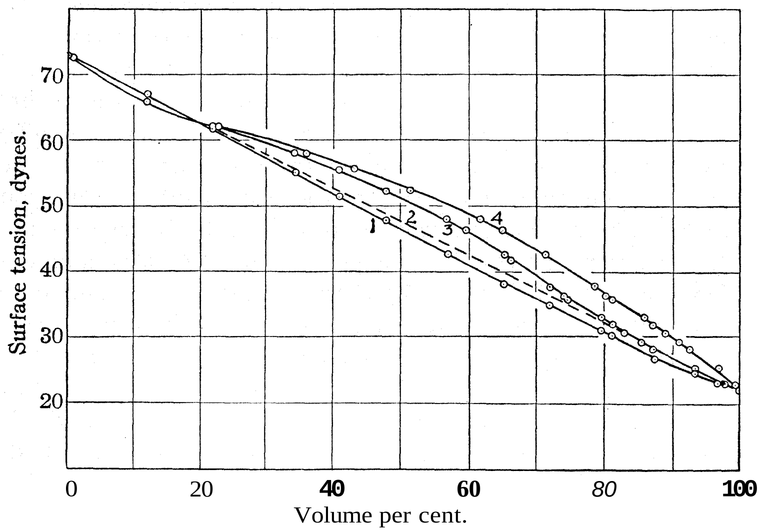

Fig. 3.—Theory of admixtures applied to surface tension of ammonia–water mixtures. 1, Surface tensions calculated by Whatmough's rule; 2, theoretical values for a perfect mixture; 3, observed values for volume per cent., $V_a/V_a + V_w$; 4, observed values for volume per cent., $V_a/V_{sol.}$.

Deviation of the ammonia–water system from the rule of admixtures might be due to adsorption of one or the other component in the surface. Assuming such to be the case, and assuming that deviation of the slope of the surface tension–log activity curve from the normal curve derived from the rule of admixtures would indicate the adsorption when used in the Gibbs equation

$$\mu = -\frac{1}{RT}\left(\frac{\mathrm{d}\ \gamma(\text{obs.})}{\mathrm{d}\ln a} - \frac{\mathrm{d}\ \gamma(\text{theor.})}{\mathrm{d}\ln a}\right)$$

such values have been assembled in Table I. They consist of from 1 to 5% of the normal surface concentration. It is of interest to note that it changes sign in the region of 50% ammonia, being negatively adsorbed in dilute solutions and positively adsorbed in the upper range of concentration.

The activities of ammonia in the mixtures were calculated by the approximate method of Lewis and Randall,[9] taking the activity equal to the concentration in pure liquid ammonia.

Summary

1. The surface tension of liquid ammonia at 0, 10 and 20°, and its temperature coefficient were determined.
2. By the differential method of Ramsay and Shields the molecular weight of liquid ammonia is found to be 24.5.
3. Surface tension and density of water–ammonia mixtures from 50–100% NH_3 at 20° are given for the first time.
4. A method is shown whereby the surface tension and density of a solution may be determined in the same sealed tube without removing the contents.
5. Surface tensions of water–ammonia mixtures follow closely values to be expected from the rule of admixtures except in the middle region, where a divergence of less than six dynes occurs.
6. Assuming divergence to be due to adsorption, it is shown that adsorption of ammonia in the surface is small, amounting from one to five per cent, of the normal surface concentration.

MANHATTAN, KANSAS

[CONTRIBUTION FROM THE DOHME LABORATORY OF PHYSICAL CHEMISTRY IN THE UNIVERSITY OF MARYLAND]

THE QUANTITATIVE PRECIPITATION OF SULFIDES IN BUFFERED SOLUTIONS.[1] I. COBALT SULFIDE

BY MALCOLM M. HARING AND MARTIN LEATHERMAN

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Introduction

The separation of metals by means of sulfide precipitation in acid or basic solution has long been practiced. However, the regulation of the degree of acidity and the conditions under which a thoroughly satisfactory precipitate may be obtained have not been the subject of much careful study. Fales and Ware[2] carefully investigated the conditions under which zinc sulfide might be precipitated quantitatively, but practically nothing else is available. Such a study on cobalt sulfide seemed desirable because the methods for the determination of this element are neither so numerous nor

[9] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923.

[1] Part of a thesis submitted by Martin Leatherman in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Maryland.

[2] Fales and Ware, THIS JOURNAL, 41,487 (1919).

satisfactory as might be wished, and because solid cobalt sulfide behaves so peculiarly when treated with acids.

Review of Literature.—Fresenius[3] and Landrum[4] both discuss the precipitation of cobalt sulfide by ammonium sulfide, but neither takes up acidity control. Both convert the sulfide to oxide and reduce the latter with hydrogen for the final weighing. Low[5] describes a method whereby cobalt sulfide is precipitated, together with nickel sulfide and traces of zinc sulfide, in a solution buffered with ammonium acetate. The cobalt and nickel mixed are weighed as oxides. No details are given as to the PH maintained, the character of the precipitate, etc.

Theoretical.—The physical character of a precipitate is conditioned, among other factors, upon the rate of formation. The latter is largely governed by the ionic concentrations concerned. Since the concentration of sulfide ion is dependent upon the hydrogen-ion concentration, the use of a buffer to control the acidity in sulfide precipitations is very desirable.

Apparatus.—The weights used were carefully calibrated. The measurements of **PH** were made using a Hildebrand type bubbling electrode. A small electric resistance furnace equipped with a silica tube was used for the roasting and reduction. Porcelain boats were used to hold the cobalt sulfide.

Materials.—The hydrogen, made by the action of zinc on 30% sulfuric acid, was purified by passage through alkaline pyrogallate, alkaline permanganate and distilled water.

The hydrogen sulfide was passed through absorbent cotton to filter out spray and then through two bottles of distilled water.

All materials were of "reagent" quality. Blanks were run on the acetic acid and ammonium acetate, and a constant weight of 0.2 mg. subtracted from all determinations to allow for the non-volatile impurities. Stock solutions of these reagents were made up in sufficient volume to permit the same solutions to be used throughout the work.

The water had a specific conductance of 2×10^{-6} mhos.

Metallic cobalt was used as the raw material in all experiments. It was purified from a good grade of $CoCl_2 \cdot 6H_2O$ by the chloropentamminecobaltic chloride method described in Biltz–Hall and Blanchard.[6] The chloride from the purification process was precipitated as sulfide, roasted and reduced with hydrogen to produce the metal in a very suitable form. No trace of nickel was detected by the dimethylgloxime method, or of iron by addition of ammonia. It had been hoped that the purified hexahydrate

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[3] Fresenius, "Quantitative Analysis," (Am. ed.), Vol. I, Section IIIC, p. 307.

[4] Landrum, *Trans. Am. Ceramic Soc.*, 12,144 (1910).

[5] Low, "Technical Methods of Ore Analysis," p. 191.

[6] Biltz–Hall and Blanchard, "Laboratory Methods of Inorganic Chemistry," 1909, p. 173.

might be weighed out directly, but it is sufficiently efflorescent to make its use inadvisable. The anhydrous form is easily made but cannot be weighed out with certainty without the most extreme precautions[7]

Discussion of Experiments

About 0.2 g. of metallic cobalt was found to be a suitable quantity for these experiments. This amount was weighed out into *a* 250 cc. beaker and dissolved in **5** cc. of concentrated hydrochloric acid. The solution was evaporated to dryness on an asbestos-covered hot-plate until all the chloride showed the bright blue color of the anhydrous salt and there was no odor of hydrochloric acid; *25* cc. of 0.4 N ammonium acetate, 40 cc. of water and sufficient 6.8 N acetic acid to produce the desired acidity were added and the ***PH*** measurement made.

Ammonium acetate was chosen as the salt of the buffer mixture used for the following reasons. Moist cobalt sulfide is readily oxidized by oxygen from the air. Hence washing with pure water will yield low results due to loss of soluble sulfate. Washing with hydrogen sulfide water is likewise inadvisable due to the tendency shown by many sulfides to peptize under such conditions. Therefore, for good results, non-volatile materials except cobalt salts should be absent at this point. Ammonium acetate is completely volatile and maintains the acidity desired and hence is eminently suitable for the purpose; 25 cc. of 0.4 *N* solution was found to provide an ample margin of safety in nullifying the effect of the acid liberated.

PH measurements could not be made with the hydrogen electrode on the mother liquor after precipitation since hydrogen sulfide poisons the electrode. The effect of the liberated acid was ascertained indirectly. Varying amounts of 6.8 N acetic acid were added to 25 cc. of 0.4 N ammonium acetate and the whole made up to 65 cc. The ***PH*** was determined, 38.6 cc. of 0.1 N hydrochloric acid was added and the ***PH*** redetermined. This quantity of hydrochloric acid is equivalent to that liberated when *0.25* g. of cobalt is precipitated as sulfide. At the ***PH*** finally selected **(3.93)** the decrease in acidity caused by precipitation was found to be *0.28* PH units. Since but 0.2 g. of cobalt was used in analysis, the decrease would be even smaller than this.

The initial ***PH*** having been determined, the solution was transferred back to the Erlenmeyer flask. The beaker and electrode washings had by this time increased the volume to about **95** cc. Hydrogen sulfide was then passed through the flask, *but not through the solution,* for about five minutes, after which the exit was closed and the pressure allowed to rise to the maximum produced by the Kipp generator. This was maintained throughout the period of precipitation. Preliminary experiments had revealed that cobalt sulfide is powerfully adsorbed by glass and that this

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[7] **Baxter** and **Coffin,** THIS JOURNAL, **28, 1580 (1906).**

adsorption is prevented by using a hot solution, by washing down the walls of the flask just before admitting hydrogen sulfide, and by having no agitation during the first few minutes of precipitation. Accordingly the solution was heated just to boiling prior to precipitation, the flask walls were immediately washed down and there was no agitation for at least the first five minutes of precipitation. Heating likewise increased the speed of precipitation and made the precipitate more compact. Giving the contents of the flask a gentle swirling motion after the earlier stages of precipitation also served to speed up this operation. The precipitation period was always continued until the contents of the flask were at room temperature (forty-five minutes to one hour). For the very low P_H values, precipitation was continued overnight. The precipitate always settled quickly, leaving a crystal clear mother liquor. At the higher P_H values precipitation was very rapid and the precipitate flocculent and very bulky. The speed of precipitation diminished with diminishing P_H, and the precipitate was very compact, forming an exceedingly thin layer in the bottom of the flask.

Filtration was carried out as expeditiously as possible. A rapid filtering, "ashless," fluted filter paper of 9 cm. diameter was used. The bulk of the precipitate and mother liquor was poured through this filter. Then the filtrate was used to wash out of the flask and onto a 3 cm. filter the remaining precipitate. In this way no liquid was poured over the precipitate after it had dried to the least extent. As stated previously, non-volatile materials should be absent at this point so that washing will be unnecessary. If this is impracticable, washing may be carried out by using as wash water a buffer solution of the same P_H as that used in precipitation, previously saturated with hydrogen sulfide and cobalt sulfide. The filtrate was always tested for cobalt by means of Vogel's test.[8] This test was found to be sensitive to 0.01 mg. of Co^{++} per 10 cc. of solution. By this means it was proved that each precipitation had been made as complete as possible under the conditions.

The procedure of Fales and Ware[2] could not be followed from this point because sulfuric acid, even when hot and concentrated, appeared to have little effect on the cobalt sulfide. Therefore instead of weighing as the sulfate it was decided to roast and reduce to the metallic state.

The filter papers and precipitate were dried at 100°, then burned in a porcelain crucible until carbon was removed. The residue was transferred to the porcelain boat, roasted at a dull red heat for half an hour, then reduced in hydrogen at 1000° for twelve to fifteen minutes, cooled in hydrogen and weighed as metal. It was found that a reduction temperature even as high as 800° was insufficient to destroy completely pyrophoric cobalt. The results of this study are displayed in Table I and Fig. 1.

[8] Treadwell, Z. anorg. Chem., 26, 105 (1901).

TABLE I

SHOWING COMPLETENESS OF PRECIPITATION OF COBALT AS THE SULFIDE FROM SOLUTIONS OF VARYING ACIDITY

Taken, g.	Found, g.	PH	Acid added, cc.	Error in parts per 1000
0.2015	0.2013	6.15	0.0	−1.0
.2360	.2357	6.15	.0	−1.2
.2035	.2034	5.17	.2	−0.5
.2015	.2012	5.18	.2	−1.5
.2005	.2004	4.40	1.5	−0.5
.1997	.1995	4.44	1.5	−1.0
.1890	.1891	4.16	3.0	+0.5
.1826	.1823	4.16	3.0	−1.6
.2022	.2021	3.93	4.5	−0.5
.2047	.2048	3.93	4.5	+0.5
.2226	.2223	3.82	5.5	−1.3
.2286	.2284	3.83	5.5	−0.9
.2109	.2107	3.72	7.5	−0.9
.2266	.2263	3.71	7.5	−1.3
.2081	.2079	3.63	9.0	−1.0
.2027	.2024	3.63	9.0	−1.5
.2007	.2003	3.52	12.0	−2.0
.2023	.2018	3.50	12.0	−2.0
.2124	.2110	3.36	16.0	−6.6
.2021	.2008	3.35	16.0	−6.4
.1795	.1634	3.09	32.5	−90.8
.1832	.1697	3.10	32.5	−70.4

As will be noted, precipitation was complete, within 0.5%, at a PH of about 3.6. No appreciable increase in error was noted at high PH values

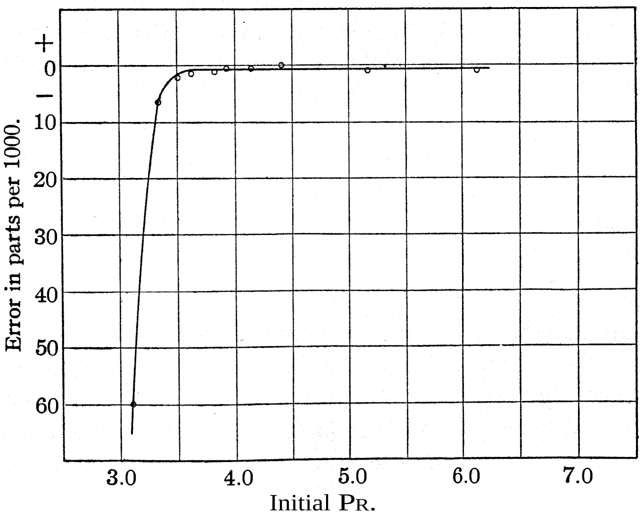

Fig. 1.—Relation between completeness of precipitation and initial acidity.

such as was found by Fales and Ware[2] with zinc sulfide. As already stated, the **PH** value selected for the quantitative precipitation of cobalt sulfide should be as low as is consistant with complete and fairly rapid precipitation. At *P*H **3.93** these conditions were met. The precipitation is complete in less than one hour and the precipitate compact and granular so that only a very small filter is needed. The **PH** values recorded in Table I are the initial values, *i.* e., before precipitation. The slight variations in PH observed between duplicates is doubtless due to the fact that there was a small loss of hydrogen chloride when the chloride solution was evaporated to dryness, To test out the method, six more determinations were made at this PH with results as recorded in Table II.

TABLE II

SHOWING ACCURACY OF DETERMINATION UNDER OPTIMUM CONDITIONS FOR PRECIPITATION AS THE SULFIDE

Taken, g.	Pound, g.	*Pa*	Acid added, cc.	Error in parts per 1000
0.2033	0.2034	3.92	4.5	+0.5
.2008	.2006	3.92	4.9	−1.0
.2066	.2065	3.94	4.5	−0.5
.2044	.2043	3.93	4.5	− .5
.2027	.2027	3.95	4.5	± .0
.2035	.2036	3.91	4.5	+ .5

It was thought that nickel and cobalt might be determined simultaneously by this method. If so, nickel could be determined separately in the metallic product by the dimethylglyoxime method and cobalt by difference. Investigation showed that nickel sulfide is precipitated practically completely at the same PH as cobalt sulfide. However, the much more highly pyrophoric nature of nickel prevented the obtaining of accurate results. This investigation is to be pursued further.

A few determinations were made to investigate the effect of concentration and the influence of ammonium salts. Although the results cannot be considered conclusive, large quantities of ammonium salts and a low concentration of cobalt ion appear to diminish somewhat the precision of the method.

Summary of the Method

Prepare an aqueous solution containing about 0.2 g. of cobalt preferably as chloride. Free acid should be absent. Add 25 cc. of 0.4 N ammonium acetate, 4.5 cc. of 6.8 N acetic acid and 70 cc. of water. Heat to boiling in a 300-cc. Erlenmeyer flask, remove from flame, wash down and saturate with hydrogen sulfide under slight pressure until the solution has reached room temperature (forty-five minutes suffices). Do not agitate for at least five minutes at the start Afterward swirl around occasionally. Pour most of the mother liquor and precipitate through a

9-cm. fluted ashless filter paper. Use the filtrate to wash out the flask and pour this and any remaining precipitate through a 3-cm. fluted ashless filter. Do not wash unless non-volatile materials are present. In this case wash with a buffer solution made up as above saturated with hydrogen sulfide and cobalt sulfide. Dry the filters in the larger funnel at 100°, fold and transfer over white glazed paper to a small porcelain crucible. Burn off filter paper by heating strongly on a quartz plate. Transfer to a weighed porcelain boat, wiping out crucible and funnel with a shred of filter paper and place in furnace. Draw air slowly through the combustion tube and start the furnace. Roast for one-half hour after the tube glows dull red. Remove tube from furnace, without cooling the latter and allow to cool for three minutes. Pass hydrogen through slowly for several minutes and replace in furnace. Heat to 1000° for fifteen minutes and remove from furnace, the hydrogen being allowed to flow until the tube is quite cold. Weigh boat and metallic cobalt.

Summary

1. A precise method has been developed for the precipitation of cobalt as sulfide and its subsequent determination as the metal.

2. The precipitation of cobalt sulfide as a function of the acidity has been studied.

College Park, Maryland

[Contribution from the Dohme Laboratory of Physical Chemistry at the University of Maryland]

THE QUANTITATIVE PRECIPITATION OF SULFIDES IN BUFFERED SOLUTIONS. II. NICKEL SULFIDE[1]

By Malcolm M. Haring and Benton B. Westfall

Received September 4, 1930 Published December 18, 1930

The quantitative precipitation of metallic sulfides as a function of the acidity of the solution has been studied systematically only in the case of zinc sulfide[2] and of cobalt sulfide.[3]

Introduction.—The latter research revealed that nickel sulfide precipitates almost completely at about the optimum P_H for cobalt sulfide. It was found also that metallic nickel, produced by the reduction of the oxide with hydrogen, was so pyrophoric as to make it difficult or impossible to weigh it in that form. The purpose of this research was to investigate more fully these two points.

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[1] Part of a thesis submitted by B. B. Westfall in partial fulfilment of the requirements for the degree of Master of Science in the Graduate School of the University of Maryland.

[2] Fales and Ware, This Journal, 41,487 (1919).

[3] Haring and Leatherman, *ibid.*, 52, 5135 (1930).

Review of the Literature.—Fresenius[4] discusses the precipitation of nickel sulfide by ammonium sulfide in solutions buffered with ammonia plus ammonium chloride or with ammonium acetate plus acetic acid. Gooch[5] gives directions for precipitation with hydrogen sulfide in the presence of an ammonium acetate–acetic acid buffer. Baubigny[6] describes the estimation of nickel in nickel sulfate by the sulfide method; Cormimboef[7] describes the precipitation of nickel sulfide in solutions "acidified sufficiently." He stresses the method of washing the precipitate. The nickel sulfide is finally roasted to the oxide.

Apparatus, Materials and Method.—The theoretical aspects of this study are the same as those discussed in the first paper of this series on CoS.[3] Likewise the apparatus, materials and general procedure remain for the most part unchanged. Platinum Gooch crucibles were used as containers for the nickel sulfide and nickel oxide instead of the porcelain boats. Silica Gooches were also found satisfactory although more fragile. These crucibles were small enough to fit snugly into the end of the silica tube so that when air was drawn through it was obliged to go through the asbestos mat. A LaMotte color comparator block with brom cresol green color standards was used in the determination of the final PH after precipitation.

The asbestos used in the Gooch crucibles was a good grade of acid-washed material prepared for this purpose. It was chipped fine, reboiled with hydrochloric acid and washed until chlorine free.

The source of the nickel was the complex ammine salt, $Ni(NH_3)_4SO_4 \cdot 6H_2O$, chosen chiefly because a large quantity of pure material was available. This had been prepared as follows. A saturated solution of recrystallized nickel sulfate hexahydrate was made in the cold. It was acidified with sulfuric acid and iron nails added to replace any copper present. Ammonium hydroxide was then added until a small amount of nickel hydroxide precipitated, and it was then aerated for about one week to remove any iron present by double displacement. The solution stood for about two weeks, being agitated occasionally, after which it was filtered. Concentrated ammonium hydroxide was then added until all the nickel hydroxide dissolved, and this mixture was allowed to stand for three days. The solution was filtered and the nickel ammine precipitated with 95% alcohol, washed with ammonium hydroxide, a mixture of equal portions of ammonium hydroxide and alcohol, alcohol, and last with ether.

A 5-g. sample, when neutralized with sulfuric acid, boiled with an excess of nitric acid and then boiled with an excess of ammonium hydroxide, gave no residue of ferric hydroxide on being filtered. A sample tested with Vogel's reagent (amyl alcohol and ether plus ammonium thiocyanate) gave no test for iron or cobalt. This is capable of detecting 0.01 mg. of cobalt per 10 cc. and the thiocyanate test for ferric iron is even more sensitive.

This salt was analyzed electrolytically (Treadwell–Hall)[8] and found to contain 22.67% of nickel. The theoretical composition gives 22.6651%.

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[4] Fresenius, "Quantitative Analysis," (Am. ed.), Vol. I, Sec. IIIC, p. 307.

[5] Gooch, "Quantitative Analysis," p. 108.

[6] Baubigny, *Compt.* rend., 94, 1183 (1882).

[7] Cormimboef, *Ann. chim. appl.*, 11, 6 (1906).

[8] Treadwell–Hall, "Quantitative Analysis," 1919, p. 147.

Description of Experiments

The efficiency of the buffer was first investigated by adding different amounts of acetic acid to a given amount of the solution containing approximately 0.2 g. of nickel as $Ni(NH_3)_4SO_4 \cdot 6H_2O$. Usually there was no ammonium acetate added as there would be approximately the equivalent of 34 cc. of 0.4 *N* ammonium acetate formed by the reaction of the acid with the salt. Acetic acid was added in excess to give the desired ***P*H**, and the ***P*H** taken, after dilution to constant volume (90 cc.), with the hydrogen electrode. The precipitation was carried out as described later, and the ***P*H** taken on the filtrate with the indicator brom cresol green. The decrease in PH during precipitation at ***P*H** 4.4 (the optimum value) was found to be 0.16 unit.

About 0.89 g. of the nickel ammine was taken for the analysis. This contained 0.2 g. of nickel, which previous experience had shown to be a sample of the most desirable size. The samples were weighed out on a watch glass and then rinsed into a 300-cc. Erlenmeyer flask. Sufficient acid was added to neutralize the ammonia and to give the desired ***P*H**. The contents of the flask were diluted to 65 cc. and the ***P*H** determined electrometrically. The volume of the solution after rinsing the electrodes was 90 cc.

Precipitation was carried out as described by Haring and Leatherman[3] except that the solution before precipitation was heated to 90°, ***not*** to ***boiling***, and the walls of the flask were not washed down. Also, just before the end of precipitation, the temperature was raised to 60°. This modification proved helpful in reducing the annoying adsorption of the nickel sulfide on the glass.

A portion of the filtrate was taken and the ***P*H** determined colorimetrically, using the comparison method. The hydrogen sulfide was boiled off the remainder and the solution tested for nickel with dimethylglyoxime.[9] When 80 cc. of the hydrogen sulfide containing filtrate was taken, as was usually the case, and evaporated to 40 cc., there was nearly always a faint pink color developed momentarily, indicating that even at the most favorable ***P*H** there was not quite complete precipitation. The test with dimethylglyoxime would indicate the presence of one part in four hundred thousand, or 0.0001 g. of nickel in the filtrate, which checks with the determination as the sulfide.

The amount of adsorption seems much more a function of the glass surface used, rather than anything else. If the glass is strained, local adsorption takes place on the strained area, whereas it may not on the rest of the surface. Of eight flasks used, two were found which gave almost no adsorption under any *P*H values used, while others gave, particularly at the upper limit, adsorption so marked that nothing short of aqua regia would remove the sulfide from the walls of the container.

An entirely new technique was developed for the operations of filtration and roasting. These were both carried out in a platinum Gooch crucible. The mat was prepared in the usual manner, but the drying was carried out at 1000°. At this temperature it was found necessary to repeat the operation of washing and drying three times in order to reach constant weight. During filtration it was found essential to keep the Gooch full of liquid at all times. Washing was unnecessary since no non-volatile materials were present. It was found impossible to destroy completely the pyrophoric character of reduced nickel, even at 1000°. For this reason the nickel was

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[9] Brunck, *Z. angew. Chem.*, *20*, 834, 3844 (1907).

TABLE I

RESULTS OF EXPERIMENTS

Taken, g.	Found, g.	Initial *Ph*	Acid added (6.8 *N*), cc.	Final *Pa*	Error in parts/1000
0.2011	0.2013	6.81	0.06	4.90	+1
.2011	.2013	6.80	.06	4.90	+1
.2013	.2012	6.59	.20	4.80	−0.5
.2012	.2011	6.59	.20	4.80	− .5
.2011	.2009	6.19	.30	4.75	−1
.2013	.2014	6.18	.30	4.75	+0.5
.2011	.2010	5.79	.34	4.70	− .5
.2011	.2010	5.79	.34	4.70	− .5
.2012	.2011	5.41	.42	4.70	− 5
.2009	.2008	5.41	.42	4.70	−
.2013	.2012	4.78	1.40	4.45	− .5
.2011	.2012	4.78	1.40	4.45	+ .5
.2012	.2010	4.51	2.20	4.35	−1
.2011	.2008	4.47	2.20	4.30	−1.5
.2007	.2005	4.34	3.00	4.20	−1
.2007	.2004	4.41	3.00	4.20	−1.5
.2013	.2009	4.08	4.45	4.05	−2
.2013	.2005	3.95	5.20	3.90	−4
.2013	.2007	3.86	6.5	3.75	−3
.2018	.2002	3.44	30.2	3.40	−8
.2014	.1915	3.30	36.5	3.30	−49.5

weighed as nickel oxide, roasting being carried out at 1000° so as to insure decomposition of any nickel sulfate. The results of this study are displayed in Table I and Fig. 1.

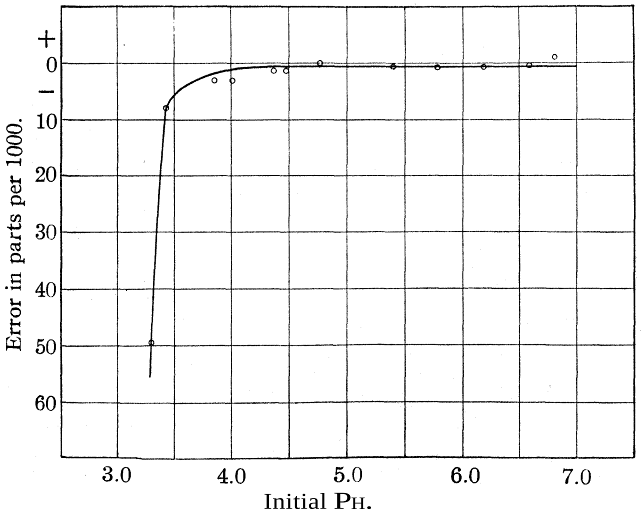

Fig. 1.—Relation between completeness of precipitation **and** initial **acidity.**

As will be evident, even at P_H 7 there is no diminution in precision. The curve reveals that the optimum P_H for nickel sulfide precipitation, *i. e.*, the lowest P_H consistent with complete precipitation and reasonable time for the same, is 4.4.

Summary of the Method

A definite quantity of the material is weighed so as to give approximately 0.2000 g. of nickel. This is dissolved in 10–15 cc. of water, the P_H is adjusted to 4.4 (the desired value) by adding 34 cc. of 0.4 *N* ammonium acetate and 2.8 cc. of 6.8 N acetic acid. The solution is then made up to a volume of approximately 90 cc. This is heated in the Erlenmeyer flask to about 90° (not to boiling). It is then connected with a source of hydrogen sulfide and the air expelled by the gas. After about five minutes the flask is rotated vigorously to aid precipitation by stirring. After precipitation the temperature is raised to 60° by heating on a water-bath. During this time it is connected to the generator. Precipitation is complete in slightly less than an hour. The solution is filtered from the precipitate by suction, using a Gooch crucible. It is very necessary that the crucible be kept full of liquid until this is complete, *i. e.*, until all the liquid and precipitate have been added. The crucible is then placed in the cold furnace and heated to 1000°, while a good current of air is drawn through, after which the crucible is cooled and weighed.

To test the method a sample of recrystallized nickel sulfate hexahydrate was analyzed for nickel content and the following results obtained.

TABLE II

RESULTS OF ANALYSES

Taken, g.	Found, g.	Initial P_H	Final P_H	Acid added, cc.	Error in parts/1000
0.1977	0.1976	4.61	4.3	2.8	– 0.6
.1975	.1975	4.53	4.3	2.8	± .0

Summary

1. A precise method has been developed for the precipitation of nickel as sulfide and its subsequent determination as the oxide.

2. The precipitation of nickel sulfide has been studied as a function of P_H.

3. Adsorption of metallic sulfides on glass surfaces appears to vary markedly with the state of strain of the glass.

COLLEGE PARK, MARYLAND

[Contribution from the Physical Laboratory, University of Denver, and the Jones Chemical Laboratory, University of Chicago]

THERMOLUMINESCENCE IN GLASSES WHICH CONTAIN TWO ACTIVATORS

By Byron E. Cohn and William D. Harkins

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Introduction

It is generally accepted that the property of luminescence may be conferred upon a solid substance by the addition of certain materials which are termed activators. The variation of luminescence with the concentration of a single activator has been studied by many workers.[1] Mathematical developments of the relation between the intensity of fluorescence and the concentration of an activator in solid solutions have been made by Brüninghaus[2] and Merritt.[3] The luminescence produced by two activators in a solid material, each acting in the presence of the other, is the subject with which this paper is concerned.

Method of Making Samples and Determination of Thermoluminescence.—The material chosen as the solid solvent was a zinc borate glass. In previous experiments[4] it had been found that a similar material could be reproduced exactly, and that activators could be uniformly dispersed within this medium. Manganese and cerium were selected as the activators because the glasses which contain them are only slightly colored, within the range of concentrations to be studied. The individual glasses were prepared as follows. To 16.5 g. of glass mixture were added the computed quantities of c. p. manganous carbonate and cerous oxalate. The glass mixture contained c. p. boric acid and zinc oxide in the ratio of six parts by weight of the former to five of the latter. These had been thoroughly mixed in a quartz pebble tube mill. The mixture for the given sample, containing the manganese and cerium salts, was placed in a covered platinum crucible and heated in a gas muffle until the molten material was entirely clear and free from bubbles. The glass was then poured into a graphite mold previously heated to 400°. The glass cast and its mold were immediately placed within an electric furnace at 400° after which the glass was allowed to cool to room temperature within the furnace. The glass was then ground and polished on the two faces until the thickness was ap-

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[1] Kowalsky and Garnier, *Compt. rend.*, 145, 391 (1907); Urbain, *ibid.*, 147, 1472 (1908); Briininghaus, *ibid.*, 149, 1375 (1909); F. Perrin, *ibid.*, 178, 1978 (1924); Engle and Hopkins, *J. Optical Soc. Am.* 11, 599 (1925); Wawilow, *Z. Physik*, 31,750 (1925); Nichols and Slattery, *J. Optical Soc. Am.*, 12, 449 (1926); Nyswander and Cohn, *ibid.*, 20, 131 (1930).

[2] Briininghaus, *Compt. rend.*, 149, 1375 (1909).

[3] Merritt, *J. Optical Soc. Am.*, 12, 613 (1926).

[4] Nyswander and Cohn, *ibid.*, 20, 131 (1930).

proximately 2.7 mm. and the small plate was cut into squares 6 mm. on a side.

The thermoluminescence of the glasses was next determined. Before each determination the samples were heated to 300° and allowed to cool to room temperature within an electric furnace to drive off any luminescence. The samples were exposed to a quartz mercury arc to excite the thermoluminescence. The glasses were exposed for ten minutes at a distance of 20 cm. from a "Lab-Arc," the latter being operated on alternating current at sixty cycle frequency and with a current of 1.50 amperes. The glasses were removed to a dark room and allowed to remain for eight hours before measurement. This precaution was taken to remove the error due to the decay of luminescence within the glass, which is quite rapid immediately after excitation. The intensity of thermoluminescence at 100° was measured by a polarization photometer with a radioactive source as the standard of intensity of the type described by Nyswander and Lind.[5] The method of measurement is described by Nyswander and Cohn.[6]

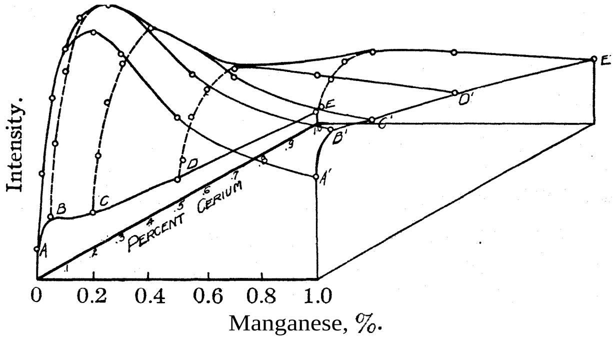

Fig. 1.—Diagram of the surface which represents the intensities of thermoluminescence of zinc borate glasses which contain both manganese and cerium, when a mercury arc is the source of excitation.

Results of Luminescence Measurements.—The intensities of thermoluminescence of a large number of samples which contain both manganese and cerium were obtained. As the intensity of the luminescence depends both upon the concentration of the cerium and that of the manganese, the intensities of luminescence when graphed form a surface. The form of surface in this case is suggested by Fig. 1. In this projection diagram the observed intensities are plotted as ordinates above the plane of concentrations. Curve A to A' represents the intensity of thermoluminescence in samples which contain 0% of cerium and varying quantities of manganese from 0 to 1%. In a like manner Curve B to B' gives the intensity in samples which

[5] Nyswander and Lind, *J. Optical Soc. Am.*, **13**, 651 (1926).

[6] Nyswander and Cohn, *ibid.*, **20**, 131 (1930).

contain 0.05% cerium and varying amounts of manganese and similarly for the remaining curves. A better representation of the actual shape of the surface which gives the luminescence is obtained from the photograph of a model, as shown in Fig. 2. In this photograph the interval between two adjacent black lines represents 0.2% change in the concentration. The zero coordinate is at the corner of the base hidden from view. It will be noted that the glass itself, though made from c. p. materials, is slightly thermoluminescent.

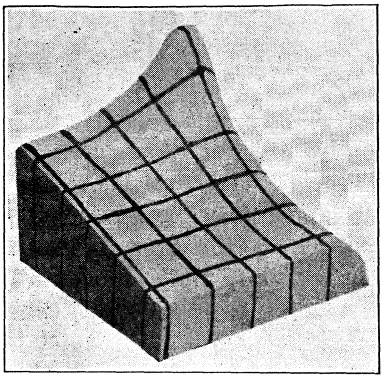

Fig. 2.—Photograph of a model of the surface indicated by Fig. 1.

Figure **3** shows the change in the intensity of the thermoluminescence of the glasses with the concentration of cerium when the concentration of the manganese is held constant. The curves represent the amounts of manganese as follows: A, 0; B, 0.02; C, 0.05; D, 0.1; E, 0.2; F, 0.5, and G, 1.0% cerium.

Figure 4 is similar to Fig. **3** except that in this set of curves the concentrations of cerium are constant for each curve. Curve **A** represents the change of the intensity of thermoluminescence with the concentration of manganese when 0% of cerium is present. The amounts of manganese are: Curve B, 0.05; C, 0.1; D, 0.2; E, 0.5, and F, 1.0%.

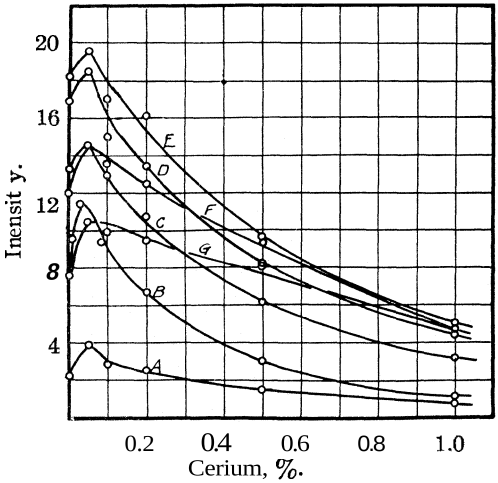

Fig. 3.—The intensity of thermoluminescence of zinc borate glasses which contain both cerium and manganese. The concentration of manganese is constant for each curve.

In Fig. 5 the intensity of thermoluminescence for glasses, each of which contains 0.02% manganese, is plotted as the ordinate and the cerium concentration of the individual glasses as the abscissa. This curve is typical of the curves for glasses which contain both manganese and cerium. It has been separated from the remaining curves of Fig. **3** for the purpose of indicating the damping action of the second activator, cerium, upon the manganese. If there were no such effect the intensity of the luminescence would approach the dotted line of the figure since the percentage of manganese remains constant; instead it falls below as indicated. The damping seems to be the same phenomenon observed qualitatively in the fluorescence of solids by Nichols and Howes[7] and discussed by them under the heading of the dominance and suppression of activators,

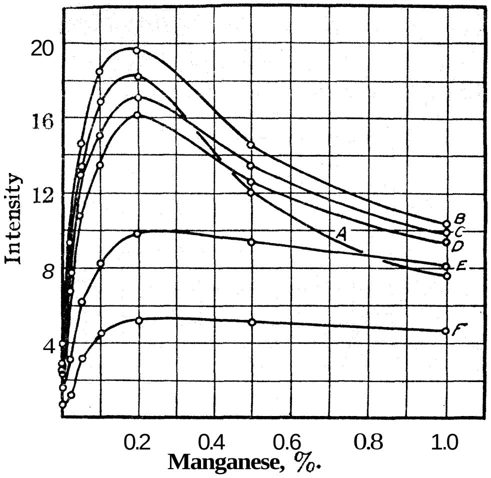

Fig. 4.—**The intensity of thermoluminescence of zinc borate glasses which contain both cerium and manganese. The concentration of cerium is constant for each curve.**

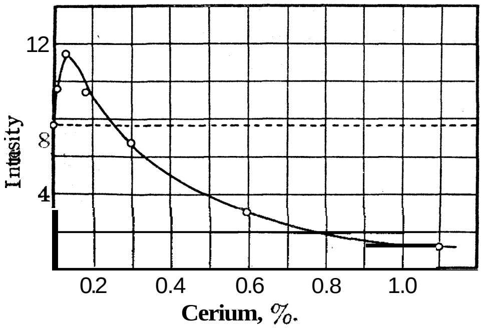

Fig. 5.—The intensity of thermoluminescence of zinc borate glasses which contain 0.02% of manganese together with cerium.

The effect of the cerium upon the luminescence of the manganese may be discussed from another viewpoint. A quantity, which will be termed the damping coefficient, will be defined as the ratio of the decrease in the intensity of thermoluminescence to the initial luminescence, when the decrease is caused by the addition of a fixed amount of the second activator. That is

$$\text{Damping coefficient} = \frac{I_1 - I_2}{I_1}$$

where I_1 is the intensity of thermoluminescence in a sample which contains manganese at a concentration A; I_2 is the intensity of thermoluminescence in a sample which contains manganese at a concentration A and cerium of concentration B. When such values are computed from the data and the damping coefficient is plotted as ordinate against the concentration of manganese (A) as abscissa, Fig. 6 is obtained. In this figure Curve A represents the damping coefficient for 1.0; B, 0.5; C, 0.2; D, 0.1; and E, 0.05%. When the damping coefficient is negative the cerium acts to increase the luminescence and therefore is an activator. It would appear from this figure that the same concentration of cerium may act either to damp the luminescence or to increase it. The effect of the cerium depends upon the concentration of the manganese. For ex-

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[7] **Nichols and Howes,** *J. Optical Soc. Am.*, 13, 573 (1926).

ample, from Curve C it is seen that 0.2% of cerium decreases the luminescence in all glasses which contain less than approximately 0.4% manganese, but acts as an activator in glasses which contain more than 0.4% of manganese. If the accuracy of the data permit the extrapolation, it would seem that the addition of 1% cerium, which decreases the luminescence of a 0.02% manganese glass to less than one-fifth its initial value, would slightly increase the luminescence in a sample which contains 2% manganese.

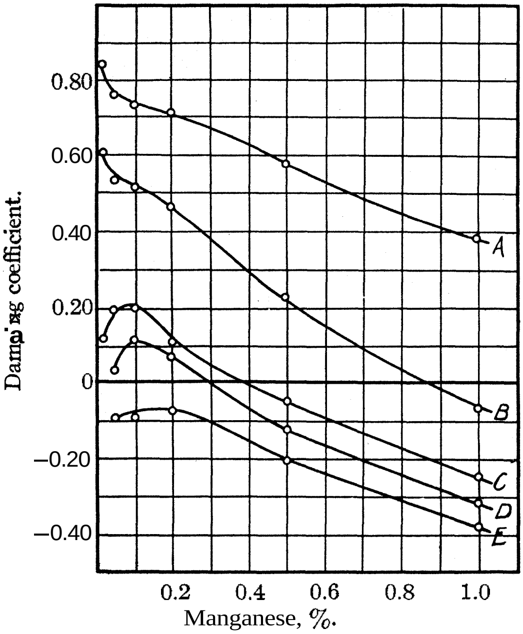

Fig. 6.—The damping coefficient as a function of the concentration of manganese in zinc borate glasses. The concentration of cerium is constant for each curve.

The Emission Spectrum of Thermoluminescence.—So far in this paper only the relative intensities of the thermoluminescent light have been discussed. Due to the low intensity of the emitted light it has not been found possible to obtain accurate spectrometric data on the thermoluminescence. However, by the use of a transmission grating, with a glowing square of zinc borate glass which contained manganese and acted as its own slit, the thermoluminescence emission was found to be a band which extends through the red, yellow and green portions of the visible spectrum. The infrared spectrum was not examined.

As the process of thermoluminescence in glasses when excited by light may be divided into the three steps: (a) the absorption of light energy, (b) the storage of the absorbed energy and (c) the emission of the stored energy, it was decided to study the absorption spectra of thermoluminescent glasses to secure more information concerning the process.

Absorption Spectra of Glasses which Exhibit Thermoluminescence.—Absorption spectra of the glasses were obtained by the use of a quartz Hilger spectrophotometer with a sector disk. The source of continuous ultraviolet light was a high frequency spark under water. The light source was constructed from the design given by Snyder.[8] From the settings on

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[8] Snyder, This Journal, 49, 2510 (1927).

the sector disk the values of the absorption coefficient K could be computed from the equation

$$\frac{I_0}{I} = e^{K\alpha d}$$

In this work I_0 is the intensity through the glass without any solute, I the transmitted intensity through glass which contains α grams of solute per 100 g. of glass and d is the thickness of the sample in centimeters. From the match point, equal density position on the spectrogram, the wave length which corresponds to K could be determined.

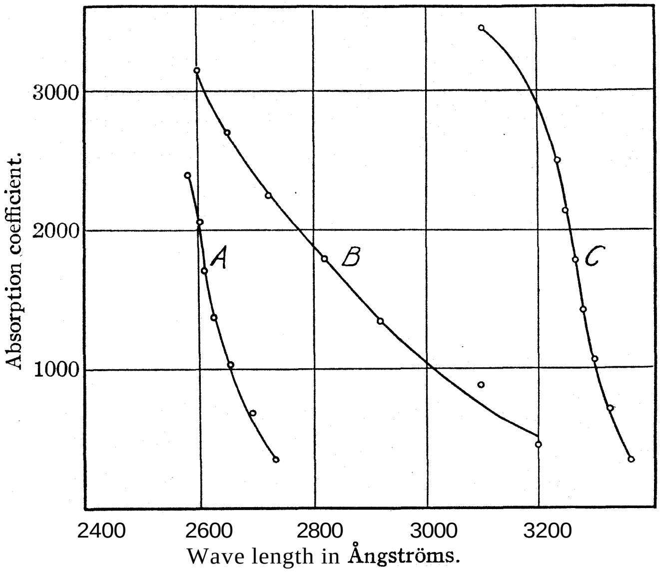

Fig. 7.—The values of the absorption coefficient K as dependent upon wave length: for zinc borate glasses which contain: Curve A, manganese; B, thorium; C, cerium.

When the values of K are plotted against the corresponding wave lengths, curves of the type shown in Fig. 7 are obtained. In this figure Curve A represents values of K obtained from a zinc borate glass which contains 0.5% manganese; B, 0.4% thorium; C, 0.5% cerium. High values of K indicate a high absorption for a given thickness and concentration. If it be assumed that these values relate to the spectral region from which the energy of thermoluminescence is absorbed, some interesting facts are indicated by the curves of Fig. 7. In the first place, absorption by these materials in glasses seems to give an absorption band only one end of which can be observed for the zinc borate glass, although a thickness of 0.27 cm. of this glass without any solute transmits well to 2500 Å., with a transmission limit close to 2400 Å. Secondly, it may be noted that for the same solvent, different light sources would show a different relative intensity of thermoluminescence for various solutes. For example, with sunlight as the source of energy, glasses which contain cerium may be expected to show a much higher intensity, relative to those which contain manganese, than when a quartz mercury arc is used as the source of excitation.

In the preceding paragraph the curves of Fig. 7 have been interpreted on the basis of the assumption that the values for K relate to the general spectral region which furnishes the energy of thermoluminescence. That this assumption has some justification is indicated by the following data. When zinc borate glass which contains 0.44% cerium was exposed to a carbon arc it was found that if the intensity of the emitted light from a square exposed directly to the source is considered to be 100, the thermoluminescent intensity from a square exposed beneath a 2.6-mm. thickness of the same glass is 3. From these values it follows that I_0/I for the exciting light which causes thermoluminescence is 33.3 and K is 3065. For this value of K in cerium glass, Curve C indicates that the mean wave length of the excitation light is 3185 Å. When the plate which gives the absorption for glass which contains 0.5% cerium is examined it is found that the absorption limit as recorded by the photographic plate varies from 3200 Å. for a ten-second exposure to 3140 Å. for a 250-second exposure. The value of 3185 A. lies within this range and seems to give some justification to the provisional assumption that the absorption boundary for which K has been calculated is the region in which the absorbed light furnishes the energy from which the energy of thermoluminescence is derived. It is hoped that this assumption can be tested with monochromatic light, but it is difficult to obtain a sufficiently high intensity.

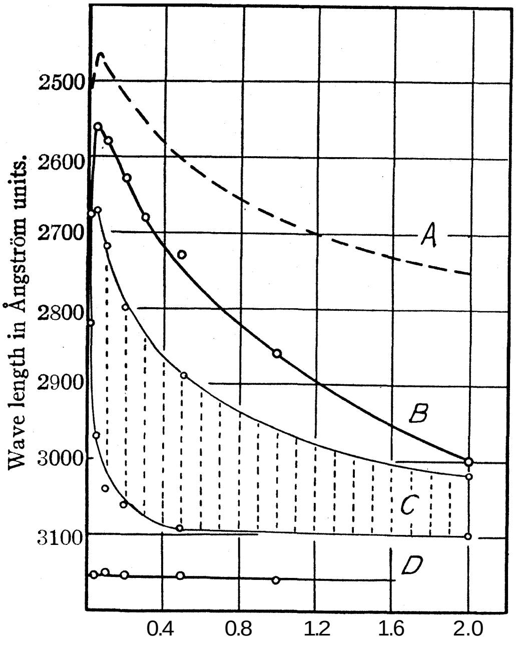

Fig. 8.—Curves B, C and D show wave lengths for which log I_0/I is equal to 0.2. Curve A represents the transmission limit for the glasses shown in curves B, C and D. Curve B represents glasses which contain zero; C, 0.02%; D, 0.05 % of cerium.

The wave lengths for which the value of log I_0/I is equal to 0.2 are shown in Curve B of Fig. 8 for zinc borate glasses which contain varying concentrations of manganese and no cerium. These are the wave lengths for which the transmission is approximately 63% of that which the glasses would have were no manganese present. If 0.02% cerium is present in addition to the manganese, the match points are definite but extend over the range indicated by the area of Curves C. With 0.05% cerium the manganese has little effect on the position of the wave lengths for which the ratio log I_0/I equals 0.2, as is exhibited by Curve D. With a sixteen-second exposure for all of the glasses, shown in Curves B, C and D, the short wave length limit of transmission obtained from the end of the spectrum on the photographic plate corresponds closely to the dotted line of Curve A. This indicates that the absorption limit of these glasses is determined by the manganese, but that the cerium determines the absorption unless the absorption is small. The form of Curve B and of Curve A, which represents the absorption limit, is unexpected.

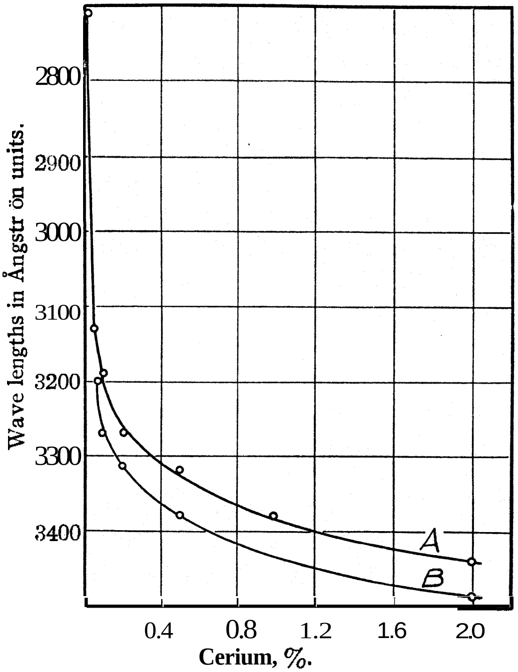

Fig. 9.—Curves which give wave lengths for which log I_0/I is equal to 0.2; Curve A represents values with zero; B, 0.02 % of manganese.

It is of particular interest since thermoluminescence is most marked in zinc borate glasses with slight concentrations of manganese and in the region affected by the anomalous absorption. Curve A of Fig. 9 gives the wave lengths for which the value of log I_0/I is equal to 0.2 for zinc borate glasses which contain varying concentrations of cerium and no manganese. If 0.02% of manganese is present in addition to the cerium, Curve B is obtained. These curves do not exhibit the anomalous behavior of the curves which represent glasses which contain manganese.

Summary

1. The thermoluminescence of glasses which contain two activators has been measured.

2. The effects of one activator upon the second are not additive. For

example, the thermoluminescence of a zinc borate glass which contains *a* small amount of manganese is increased by small amounts of cerium, but decreased by larger amounts. A definite amount of cerium may either increase or decrease the thermoluminescence, since the effect is dependent upon the amount of manganese present.

3. The emission spectrum for zinc borate glass which contains manganese has been found to be a band.

4. Single ended absorption bands have been found in the ultraviolet spectra with zinc borate glasses which contain manganese, cerium or thorium as the solute.

5. Intensity measurements of the thermoluminescence have been used to indicate that it is probably from near the edge of these bands that the energy for thermoluminescence is drawn.

6. From the positions of the absorption bands the conclusion is drawn that the relative thermoluminescent intensities of two materials in the same solvent changes with a change of the source of excitation.

7. Absorption curves which show the effect of cerium upon glasses which contain manganese and vice versa have been obtained.

8. An anomalous absorption has been found for zinc borate glasses which contain manganese.

DENVER, COLORADO

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY, UNIVERSITY OF PENNSYLVANIA]

STUDIES ON HETEROPOLY ACIDS OF GERMANIUM. I. GERMANOMOLYBDIC ACID[1]

BY CHARLES G. GROSSCUP

RECEIVED SEPTEMBER 18, 1930 PUBLISHED DECEMBER 18, 1930

In the list of elements known to form heteropoly acids with molybdenum, tungsten and vanadium, one notices the absence of three members of the fourth periodic group. These elements, carbon, germanium and hafnium are missing from an otherwise complete series of the type $H_8[X(Mo_2O_7)_6]$ aq. where X may be silicon,[2] titanium,[3] zirconium,[3] thorium,[4] tin[6] and lead.6 Possibly this may be supplemented by hafnium, which, it is conceivable, was present in the preparations of zirconomolybdates, since this element was not recognized at the time of the investigations and has since

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[1] An extract from a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Pennsylvania.

[2] A pure acid has been obtained by Scroggie, THIS JOURNAL, 51, 1057 (1929).

[3] Péchard, *Comfit. rend.*, 117, 781 (1893).

[4] Barbieri, *Atti. accad. Lincei*, **221**, 5, 781 (1913).

[5] Rosenheim, Pieck and Pinsker, Z. *anorg. Chem.*, 96, 139 (1916).

[6] Ephraim, "Inorganic Chemistry," English ed., 1926.

been proved to be present in specimens of supposedly pure zirconium compounds to the extent of as much as 5%. Other elements exhibiting tetravalency such as manganese,[7] platinum[6] and cerium[8] may also be included here. The elements grouped about germanium in the periodic system, especially boron, phosphorus and arsenic, are known to play the role of central atom in similar compounds, *e.* g., the familiar ammonium phosphomolybdate, $(NH_4)_3H_4[P(Mo_2O_7)_6]$ aq.

The similarities in chemical behavior of germanium to arsenic and silicon were largely responsible for the present endeavor to prepare a heteropoly acid which would be the germanium analog of silico-duodecimomolybdic acid, $H_8[Si(Mo_2O_7)_6]\cdot 28H_2O$. That germanium would enter into such "poly acid" formation was a logical conclusion and is supported by the results of this paper. A knowledge of "complexes" is important from an analytical standpoint, since the identity of the constituents of certain compounds and mixtures may be so masked that the elements escape detection in the usual procedures and the analyst is confronted with unusual reactions. It is through a study of the formation and properties of these compounds that the unexpected behavior of certain elements in the presence of molybdic, tungstic and vanadic acids is to be anticipated and means taken to insure their detection.

Experimental

Materials.—The germanium dioxide was prepared from zinc residues which were kindly furnished by Professor J. H. Müller. It was of the highest purity and entirely free from arsenic. The molybdenum trioxide was Baker's "Special," free from arsenic and phosphorus. Lead, calcium, magnesium and ammonium salts, sodium hydroxide, hydrobromic acid and sulfuric acid (special arsenic free) were Baker chemicals. Reagent quality ether was distilled over sodium. Guanidine carbonate was obtained from the Eastman Kodak Co. Laboratory distilled water was redistilled for preparation work. Ammonium hydroxide was redistilled in pyrex vessels and used immediately.

Preparation of the Free Acid.—Five grams of germanic oxide was dissolved in 200 ml. of water containing 7 g. of sodium hydroxide and the solution brought to boiling, whereupon 70 g. of molybdic oxide was slowly added with stirring. Rapid solution of the molybdic oxide took place until about half the amount had been added. Almost complete precipitation occurred at this point, followed by re-solution with continued addition of the molybdic oxide. An intense yellow color developed after this midpoint of reaction. Gentle boiling was continued for five minutes, the solution filtered and allowed to cool. The method of extraction was that of Drechsel;[9] several hundred ml. of ether was added, followed by an excess of cold 9 *N* sulfuric acid. An intermediate turbidity disappeared when sufficient acid had been added. Heavy yellow oily drops separated and settled, forming the third layer common to such extractions. This lower layer—an ether solution of the "complex acid"—was removed and evaporated at 40°. After powdering, the residue was dissolved in a small volume of water and the extraction with ether and sulfuric acid repeated. The ether was removed as before, the residue

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[7] Péchard, *Compt. vend.*, **125**, 29 (1897).

[8] Barbieri, *Atti accad. Lincei*, **23i**, **5**, 805 (1914).

[9] Drechsel, *Ber.*, **20**, 1452 (1887).

dissolved in water, the solution filtered and then allowed to crystallize at room temperature (18–28°). The major portion of mother liquor was removed by filtration and the crystals dried as rapidly as possible by pressing between filter paper, after which they were kept in tightly stoppered weighing bottles or weighed out at once for analysis. In spite of the high solubility, the solutions crystallized well. Three separate batches of the acid were prepared.

Preparation of the Guanidine Salt.—To an aqueous solution of the acid was added a concentrated solution of guanidine carbonate, the mixture warmed and filtered. The residue was boiled with water until solution was nearly complete, then filtered and cooled. The shining greenish-yellow crystals were removed and dried at 105°. On standing for several days the filtrate deposited white crusts containing germanium and molybdenum.

Properties.—The free acid crystallizes in yellow transparent octahedra, readily efflorescing. The melting point is approximately 65". Induration, with loss of color and transparency, invariably resulted from attempts to preserve crystals imperfectly freed of mother liquor. Such changes took place in a few days and the substance produced, in sharp contrast to the parent compound, was but sparingly soluble in water. Well-dried specimens on the other hand have been kept ten weeks, suffering no apparent deterioration and differing from fresh samples only in a slightly lower water content Analogous to the behavior of the corresponding silicon compound, pale yellow, difficultly soluble compounds are obtained with silver, thallous, mercurous, cesium, rubidium and guanidine salts and with alkaloids.

Analysis.—Calibrated weights were used and all gravimetric determinations were brought to constant weight (±0.05 mg.).

A. **Water.**—Samples were dried in an oven at 105° for "water of hydration." Total loss on ignition was determined by heating at 400° in a resistance furnace. The residues were yellow when hot and pale blue when cold.

B. Germanium and Molybdenum.—A number of separations were tried but only one yielded duplicable results. The procedure finally adopted was a distillation from 9 *N* hydrobromic acid. The free acid or ignition residue was placed in a 200-ml. round-bottomed flask, to which was attached by a ground joint a 25-cm. neck with side arm. A meter length of glass tubing dipping under water in an Erlenmeyer flask served as a condenser and receiver for the germanium tetrabromide; 25 ml. of hydrobromic acid (sp. gr. 1.30) containing a small amount of bromine was added to the flask and the mixture slowly distilled. If less than two hours were consumed in this operation, a little molybdenum usually appeared in the distillate as evidenced by the brown color of the sulfide. The distillation was continued until the volume of the solution remaining in the flask was about **3** ml.; an additional 25 ml. of hydrobromic acid was introduced and the distillation repeated. The distillate was made 6 N in acid by adding concentrated sulfuric acid and the germanium precipitated as sulfide by saturating the hydrogen sulfide. The germanium sulfide was filtered on a Konig crucible and, after washing with 6 N sulfuric acid saturated with hydrogen sulfide, was converted to oxide by nitric acid in the usual manner. The brown solution remaining in the distilling bulb was washed into a small sillimanite crucible, ten drops of concentrated sulfuric acid added and this mixture evaporated to dryness in an air-bath. The residue was gently ignited to expel sulfur trioxide and weighed as molybdic oxide.

C. The guanidine salt was analyzed for nitrogen by the Dumas method.

Discussion

Three physical constants of the compound under investigation suggested a formula similar to silicomolybdic acid, $H_8[Si(Mo_2O_7)_6]$ aq. They are:

(1) the isomorphism of the free acids; (2) the yellow color, which is usually associated with "poly acids" containing Mo_2O_7 groups; **(3)** the melting point, which is comparable with the values for the silico acid, 45°, and the titano acid, 60°.

The theoretical composition of $H_8[Ge(Mo_2O_7)_6]$ aq., according as the amount of "aq." is 24, 25, 26 and 28 moles, respectively, is given in Table I.

TABLE I

THEORETICAL COMPOSITIONS

	24 aq.	25 aq.	26 aq.	28 aq.
Ignition loss	21.58	22.18	22.77	23.92
GeO_2	4.48	4 44	4.41	4 34
MoO_3	73.94	73.38	72.82	71 74
	100.00	100 00	100.00	100.00
"aq."	18.48	19.02	19.72	21.58
Molecular weight	2336.6	2354 6	2372 6	2408 6

The tendency of the crystals to effloresce made it difficult to obtain samples of exactly the same composition, although the deviation and variance of results is not great, *as* is evident from the analyses.

TABLE II

"AQ." AND IGNITION LOSSES

No.	Sample, g.	Loss at 105°, %	Ignition loss, %
1	0.46224	19.26	22.41
2	.37547	19.10	22.65
3	.20490		22.20
4	.17245		22.31
5	.17857		22.19
6	.59183		22.47
7	45747		22.62
8	.57261		22.32
9	.38234		21.77
10	.30670	18.70	21.88
11	.31427		22.15
12	.25630		22 08
13	.18382		22.08
14	.11287		21.18
15	.14546		21.22
16	.13040		21.20

Samples 1–5 from Preparation **A**; samples 6–10 from Preparation B; samples 10–16 from Preparation *C*; samples 14, 15, 16 were kept for ten weeks before analysis.

It will be seen that the ignition losses predicate an "aq." content of 24–26 moles and that the values for loss at 105° are in proportionate agreement. The molecular formula for silicomolybdic acid is accepted as $H_8[Si(Mo_2O_7)_6]\cdot 28H_2O$ but the analysis of the germanium compound failed to reveal a water content of the same magnitude. Five of the above samples were analyzed by the hydrobromic method and gave the following values.

TABLE III

ANALYSIS OF THE FREE ACIDS

No.	2	6	12	8	9
Wt. of sample, g.	0.37547	0.59183	0.25630	0.57261	0.38234
MoO_3 found, g.	.27177	.43085	.18761	.42087	.28217
MoO_3, %	72.38	72.80	73.20	73.50	73.80
GeO_2 found, g.	0.01633	0.02604	0.01164	0.02548	0.01759
GeO_2, %	4.35	4.40	4.54	4.45	4.60
Ignition loss, g.	22.65	22.47	22.08	22.32	21.77
Total	99.38	99.67	99.82	100.27	100.17
Ratio $GeO_2:MoO_3$	1:12.07	1:12.01	1:11.72	1:12.00	1:11.65
Ratio GeO_2 $MoO_3:H_2O$	1:30.10	1:29.68	1:28.92	1:29.25	1:28.22

Since vapor pressure measurements were not made, the existence of lower hydrates is not postulated. By efflorescence, however, it is conceivable that samples could have compositions agreeing with those selected in Table I.

Because of the simplicity of procedure we may use the ignition loss as a standard in the critical examination of results. Comparing, for example, Analyses 2 and 6, we see that lower ignition loss in No. 6 is compensated for by a higher metallic oxide content and, by reference to Table I, that the values for ignition loss, MoO_3 and GeO_2, agree proportionately within the limits of experimental error.

North and Beal[10] made use of a titration with sodium hydroxide as a means of analysis for silicomolybdic acid. Scroggie[2] repeated the work, using chlor phenol red as indicator. The complete decomposition of the germanium compound by alkalies may be expressed by the equation

$$GeO_2 \cdot 12MoO_3 \text{ aq.} + 24\,NaOH = GeO_2 \text{ aq.} + 12\,Na_2MoO_4 + \text{aq.}$$

if the germanic acid is not attacked under the conditions of the experiment. A sample, No. 13, after ignition was titrated with 0.2920 N sodium hydroxide and chlor phenol red. The water content, 22.08%, corresponds closely with that of $H_8[Ge(Mo_2O_7)_6] \cdot 25H_2O$, with a molecular weight of 2355. On this basis the titration required 23.93 moles of sodium hydroxide per mole of acid. Calculated from the weight of ignited oxides the value is 23.95. Another sample, No. 17, wt. 0.15717 g., was weighed out at the same time as samples No. 6 and No. 7, the water content of which gave a mean value of 22.54%, approximately equivalent to $H_8[Ge(Mo_2O_7)_6] \cdot 26H_2O$. Assuming then a molecular weight of 2373, the titration showed a consumption of 23.80 moles of the base.

That progressive decomposition with the intermediate formation of "unsaturated" compounds—those with lower MoO_3 content—took place was indicated by the fact that upon the addition of a drop of the base the basic color of the indicator persisted several minutes and then gradually

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[10] North and Beal, *J. Am. Pharm. Assn.*, 13,889 (1924).

faded. The titration was necessarily extended over a period of several hours before a permanent "end-point" was reached.

The analysis of the guanidine salt gave 7.97% nitrogen. The theoretical value for the tetrabasic salt, $(CN_3H_5)_4H_8[Ge(Mo_2O_7)_6]$ is 7.84%.

The product resulting from the deterioration of the undried crystals was washed with hot water, air dried and analyzed.

Table IV

Analysis of White Insoluble Compound

Water at 105°, %	0.00
Ignition loss, %	11.20
MoO_3, %	86.50

Lack of material prevented a further study. Disruption of the original molecule apparently took place and a portion of the germanium was removed in the washing operation.

While the deviations from theoretical values are at times large, yet the results indicate the existence of a heteropoly acid of germanium and molybdenum with the formula $GeO_2 \cdot 12MoO_3 \cdot aq.$, which may be written, after the fashion of the Miolati system of constitution, as $H_8[Ge(Mo_2O_7)_6]aq.$, a member of the series $H_{12-n}[X_n(Mo_2O_7)_6]aq.$ The coefficient for the "aq." has an apparent maximum of 26. The seriousness of the deviations is somewhat mitigated if one considers that ammonium phosphomolybdate, used since the time of Berzelius in analytical procedures, is, because of somewhat indefinite composition, still unsuited for gravimetric work.

In accordance with the present system of nomenclature the new compound may be called 12-germanomolybdic acid or germano-duodecimo-molybdic acid.

The ease of formation of germanomolybdic acid and its salts makes the compound susceptible to qualitative and perhaps quantitative application for the detection and determination of germanium. To this purpose, germanium sulfide—the usual form in which the element is isolated—can be converted into the oxide and this boiled with a small volume of water and some molybdic oxide. The presence of the germanomolybdic acid thus produced may be confirmed by color or precipitation reactions. A yellow color is easily seen when 0.00183 g. of the free acid (corresponding to approximately 0.000082 g. of germanic oxide) is dissolved in 5 ml. of water. This may prove of particular value since no colorimetric determination of germanium has been reported.

Summary

1. The preparation and properties of a heteropoly acid of germanium and molybdenum of the type $H_8[Ge(Mo_2O_7)_6]$ aq. is outlined.

2. The use of the new acid and its salts for the colorimetric determination of germanium is suggested.

PHILADELPHIA, PENNSYLVANIA

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

NITROGEN COMPOUNDS OF GERMANIUM. I. THE PREPARATION AND PROPERTIES OF GERMANIC NITRIDE

BY WARREN C. JOHNSON

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According to the literature silicon[1] combines directly with nitrogen, when heated at 1300 to 1450°, to form the normal nitride, Si_3N_4. A similar reaction takes place when this element is heated in an atmosphere of ammonia at high temperatures. Analogous reactions in the case of germanium, tin and lead are lacking.

Carbonic anammonide, $(C_3N_4)_x$, has been obtained[2] as a highly polymerized, orange powder by heating mercuric thiocyanate. Pauly[3] has reported $(C_3N_2)_x$, carbonous nitride or anammonide, as being obtained by the thermal decomposition of tetra-iodo-imidazole. This has since been shown[4] in all probability to be a mixture of carbon and paracyanogen, $(C_2N_2)_x$. Bergstrom[6] prepared stannous imide, SnNH, by reacting potassium ammono stannite, SnNK, with a solution of ammonium bromide in liquid ammonia. The imide was deammonated by heating in a vacuum at 340°. The reaction resulted in the formation of stannous anammonide or nitride, Sn_3N_2. This nitride is the only definite one known of the fourth outer group elements exhibiting a valence of two. Carbonic nitride and silicic nitride are the only representatives of these elements functioning with a valence of four.

Recently Schwarz and Schenk[6] studied the ammonolysis of germanium tetrachloride in liquid ammonia solution. Their results indicate that the hexammonate described by Thomas and Pugh[7] may not exist in liquid ammonia. Schwarz and Schenk allowed germanium tetrachloride to ammonolyze, separated the ammonium chloride and found a definite combination in the imide, $Ge(NH)_2$. At 150° the imide was found to lose ammonia with the formation of the germanam, Ge_2N_3H. This latter

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[1] Weiss and Engelhardt, Z. *anorg. Chem.*, 65, 78 (1910); Funk, *ibid.*, 133, 67 (1924).

[2] King and Chamberlain, "Theses," Stanford University, 1924, and 1930, respectively.

[3] Pauly, *Ber.*, 43, 2243 (1910).

[4] Wenzel, "Dissertation," Stanford University, 1927.

[5] Bergstrom, *J. Phys. Chem.*, 32, 433 *(1928).*

[6] Schwarz and Schenk, *Ber.*, 63, 296 (1930).

[7] Thomas and Pugh, J. *Chem. Soc.*, 1051 (1926).

combination was found to be stable at 300° but at higher temperatures to decompose, with loss of ammonia, to the nitride, Ge_3N_4. Their evidence for the formation of the nitride is based entirely upon the changes in weight resulting from the decomposition of the germanam and of the imide; no analyses are reported to substantiate the existence of germanic nitride. In the case of the decomposition of the imide the ammonia liberated was determined. Since these changes in weight are very small, especially when minute quantities of the substances are used, it is difficult to state the purity of the nitride without analytical data on the germanium and nitrogen content. However, it is the belief of the writer that Schwarz and Schenk have prepared germanic nitride.

Before the work of these investigators appeared, Kraus and E. G. Johnson[8] studied the ammonolysis of germanium tetrachloride. Their results are in agreement with those of Schwarz and Schenk in the formation of the imide and the germanam, and definitely substantiate the existence of the nitride.

The following described investigation confirms the results of the above-mentioned workers in that germanic nitride is prepared by the action of ammonia gas on metallic germanium at elevated temperatures. Some of the physical and chemical properties of the nitride are also determined.

Experimental

Source of Material.—The germanium was obtained as germanous sulfide from germanite ore according to the procedure described by Kraus and Johnson.[9] The sulfide was oxidized with nitric acid to germanic oxide, which was then reduced with hydrogen at 600° to the gray germanium powder. For purification, the metal was heated in a stream of chlorine gas at 250' to form germanium tetrachloride, the chloride was hydrolyzed to the oxide, and finally the oxide was again reduced with hydrogen to germanium. This procedure gave germanium in a finely divided state and of fairly high purity.[10]

Anhydrous ammonia of commerce was siphoned from its container into a small steel cylinder containing several small pieces of sodium, which served to remove the water completely. During the course of a reaction the ammonia was allowed to escape from this cylinder as a gas.

Preparation of Germanic Nitride

(a) The Action of Ammonia on Germanium.—A weighed amount of the powdered germanium, obtained from the reduction of germanic oxide, was placed in a weighed alundum boat in a vitreosil tube. The tube extended horizontally through an electric

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Kraus and E. G. Johnson, Brown University, private communication.

Kraus and Johnson, Paper given at the Swampscott Meeting of the American Chemical Society, September, 1928.

[10] It has been shown by Dennis, Tressler and Hance, THIS JOURNAL, 45, 2034–5 (1923), that small amounts of germanium dioxide may be reduced quantitatively with hydrogen, but when several grams of the oxide are used, the reduction does not appear to be complete. This fact accounts for the low yields of germanic nitride obtained in the following described experiments.

furnace the temperature of which was measured with a thermocouple. A fairly rapid stream of ammonia gas was allowed to pass over the germanium at different temperatures. A slow reaction was observed at 650"; at 700° the formation of nitride appeared to be quite rapid, only three hours being required to convert 1 g. of germanium to the nitride. The samples of germanium were heated in an atmosphere of ammonia until no increase in weight of the boat was observed to indicate the continued formation of nitride. The nitride appeared as a light brown powder.

The following data show the formation of germanic nitride.

Ge, g.	Ge_3N_4 (obtained), g.	Ge_3N_4 (calcd.), g.
0.4603	0.5756	0.5787
4.2852	5.3718	5.3878

When ammonia was passed over germanium at temperatures in the neighborhood of 850" and above, no nitride was formed. Since, as was found in later experiments, the nitride is readily reduced with hydrogen at elevated temperatures, the absence of its formation at 850° is readily accounted for by the high concentration of hydrogen present in the gas mixture due to the dissociation of ammonia.

(b) The Action of Ammonia on Germanic Oxide.—Ammonia was found to react slowly with germanic oxide at 700° and much more rapidly at 750°. The ammonia served to reduce the oxide to germanium, which in turn reacted with additional ammonia as described above. The probable course of the reaction is

$$3GeO_2 + 4NH_3 = Ge_3N_4 + 6H_2O$$

The formation of the nitride in this reaction was indicated by the light brown color and the following changes in weight.

GeO_2, g.	Ge_3N_4 (obtained), g.	Ge_3N_4 (calcd.), g
0.4808	0.4188	0.4195
4.1299	3.6074	3.6039

The Reduction of Germanic Nitride. The Determination of Germanium and Nitrogen.—Preliminary experiments showed that the usual methods for the determination of nitrogen were not highly satisfactory. Concentrated sulfuric acid and also a mixture of this acid with concentrated nitric acid reacted slowly with the nitride even on boiling. Several days were required to dissolve a small amount of the nitride when this procedure was followed. A concentrated solution of sodium hydroxide, even when boiled, did not liberate ammonia and appeared to have no effect on the nitride. It was found, however, that, when the nitride was heated at a temperature as low as 600° in a stream of hydrogen gas, reduction took place readily to metallic germanium and ammonia. At 700° the reduction process was found to be extremely rapid. The reaction evidently proceeds as follows

$$6H_2 + Ge_3N_4 = 3Ge + 4NH_3$$

Likewise, the reaction to the left expresses the process for the formation of the nitride from germanium and ammonia.

In collecting the ammonia resulting from the reduction of the nitride, the gas stream was allowed to pass through two wash bottles containing a known amount of standard hydrochloric acid solution. The strength of the acid was 0.1032 N. When the reduction was completed, the solutions were titrated back with standard sodium hydroxide solution and the amount of acid used to combine with the ammonia was calculated accordingly. The residue remaining in the boat after complete reduction of the nitride was germanium in the elementary state.

Quantitative results were obtained in this procedure when a rapid stream of hydrogen was used so that the ammonia would be rapidly swept out of the hot regions of the furnace. A slow gas stream permitted the ammonia to dissociate into nitrogen and hydrogen and low results were obtained.

The results of the reduction are given in Table I. In the first column is given the weight of germanic nitride reduced, in the second and third columns, the weight of germanium found in the boat after complete reduction and the theoretical amount, respectively; in the fourth, the volume of standard acid solution used to neutralize the ammonia collected; and in the fifth and sixth columns, the amount of nitrogen as calculated from the titration and the theoretical amount, respectively.

TABLE I

ANALYSIS OF GERMANIC NITRIDE FOR GERMANIUM AND NITROGEN

Ge_3N_4, g.	*Ge* (found), *g.*	*Ge* (calcd.), g.	HCl, cc.	N_2 (found), g.	N_2 (calcd.), *g.*
0.5000	0.3989	0.3977	70.17	0.1020	0.1023
.6586	.5270	.5238	91.14	.1318	.1348
.5732	.4553	.4559	82.65	.1195	.1173

The Oxidation of Germanic Nitride.—Germanic nitride was found to be exceedingly stable toward the usual oxidizing agents. Even a mixture of fuming nitric and fuming sulfuric acids caused only a slow oxidation on boiling. When the compound was heated in air at the temperature of the Méker burner, oxidation took place with difficulty. Pure oxygen gas was found to oxidize the nitride at 850–900°; on the other hand, the reaction proceeded slowly at 800°. White germanic oxide was formed in this reaction; the condition of the nitrogen was not determined but, without doubt, it was eliminated as elementary nitrogen.

Anal. Subs., 0.5766, 0.9777. Calcd. GeO_2: 0.6607, 1.1203. Found: 0.6593, 1.1180.

The Chlorination of Germanic Nitride.—Germanic nitride, 0.4321 g., was weighed in an alundum boat which was introduced into a vitreosil tube. A slow stream of chlorine gas, emitted from a tank and dried with concentrated sulfuric acid, was allowed to pass over the nitride at different temperatures. The temperature was controlled as previously described. The first heating was carried out at 400–450° for a period of two hours; only 2.3 mg, loss in weight resulted. When the temperature was increased to 600° for four hours, more than one-third of the material was found to have left the boat. The color of the remaining material was brown, but of a little lighter shade than that of the original sample. The heating was continued for several hours at temperatures ranging from 500–575° but no indication of reaction was found; however, at 600–700°, the reaction proceeded rapidly, as all but 50 mg. of the original sample of the nitride disappeared from the boat during a four-hour heating. The color of the remaining nitride was still a light brown. It was found possible, on further heating at the last-named temperature, completely to remove the nitride from the boat by the reaction with chlorine gas. Germanium tetrachloride was observed as one of the products of the reaction. The following equation expresses the probable course of the reaction

$$Ge_3N_4 + 6Cl_2 = 3GeCl_4 + 2N_2$$

Color.—Schwarz and Schenk state that germanic nitride is white when pure. In the decomposition of their germanam they obtained a brown colored nitride, but they attribute the color to the presence of finely divided germanium. In view of the above-described experiment on the chlorination of the nitride, it is impossible to ascribe the color to any appreciable amount of metallic germanium. Germanium is well known to react with chlorine readily at temperatures as low as 100°.

In the above, the brown color persisted after the nitride had been heated for many hours in chlorine at temperatures ranging from 400–700°. If any germanium were present with the nitride, one would expect it to be quickly removed as germanium tetrachloride, which is thermally stable at the temperatures of the experiments. Since the brown color did appear to vary in intensity in the different preparations and since the chlorine rendered them lighter in color, undoubtedly a small amount of germanium was present. This amount is accounted for in the first loss in weight recorded in the chlorination experiment, namely, 2.3 mg., but no loss resulted when the same material was later heated at 500–575°. On the other hand, the persistence of the color throughout the entire reaction either means that the nitride is normally a light brown or that another constituent is present, possibly germanium or a lower nitride, which is so finely dispersed throughout the mass of the material as to render its separation difficult.

The presence of an appreciable amount of germanous nitride[11] with the germanic nitride is not substantiated by experiments. This nitride is quite volatile and would be removed from the germanic nitride at the temperatures required for the preparation of the latter.

It may also be suggested that the color is due to the polymerization of the germanic nitride molecule.

The Dissociation of Germanic Nitride.—The decomposition of the nitride at 900–1000° resulted in the production of germanium and nitrogen. (A small amount of material, black to brown in color, appeared on the walls of the tube. This is thought to be germanous nitride.)[12] The results obtained by Schwarz and Schenk at the high temperatures are confirmed in this experiment. It should be stated, however, that in our experiments the nitrogen was removed rapidly by means of a Hyvac pump while the dissociation proceeded.

When the nitride was decomposed in a closed system at lower temperatures, 600–700°, a considerable amount of material collected on the walls of the tube in the cooler regions. The pressure developed by the nitrogen was measured at different intervals over a period of several weeks and was found to increase gradually. There was no indication of any equilibrium values. If dissociation at this temperature produces nitrogen and germanium, there must necessarily result some germanous nitride, which would volatilize and collect on the walls of the tube. It will be necessary to study the dissociation of germanic nitride under dif-

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[11] Germanous nitride, Ge_3N_2, has been prepared in this Laboratory by Mr. J. R. Hart. It is formed readily when metallic germanium is heated in nitrogen at 800–950°. Thin layers of this nitride appear brown in color while the substance in a compact form appears black. It is readily volatile at a temperature as low as 650°. The results concerning its preparation and properties will appear in a forthcoming publication.

[12] Observations by Mr. J. R. Hart.

ferent conditions, and, if possible, to obtain equilibrium values before any definite statement may be made concerning the mechanism of the process.

Other Properties.—Germanic nitride resembles the corresponding compound of silicon in its remarkable stability. It is not affected by air at ordinary temperatures. It is insoluble in water and all the common inorganic solvents. It is not attacked by water at 100°. A boiling solution of sodium hydroxide does not liberate nitrogen as ammonia from the nitride. Strong acids appear to affect it slightly.

Summary

Germanic nitride has been prepared by reacting metallic germanium with ammonia gas at 700°. Germanic oxide may be used in place of germanium in this reaction.

The nitride is readily reduced by hydrogen at 700° to germanium and ammonia. This process serves as a method of analysis for the germanium and nitrogen.

The oxidation of the nitride to germanic oxide by means of oxygen at 850° proceeds rapidly. Chlorine gas reacts with germanic nitride at high temperatures.

The color, dissociation and other properties are discussed.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM TEE GEORGE HERBERT JONES CHEMICAL LABORATORY OR THE UNIVERSITY OF CHICAGO]

A SPECTROSCOPIC STUDY OF THE DECOMPOSITION AND SYNTHESIS OF ORGANIC COMPOUNDS BY ELECTRICAL DISCHARGES. I. THE ELECTRODELESS DISCHARGE

BY WILLIAM D. HARKINS AND DAVID M. GANS

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1. Introduction

While the effects of electrical discharges upon organic gases and vapors have been investigated extensively, little has been known concerning the mechanism of their action. Thus the final condensation products have been studied, but there has been practically no knowledge of the decomposition products formed initially in the discharge.

In certain respects the conditions in low voltage discharges resemble those in flames, although the velocities of the free electrons are commonly greater in the former. In flames produced by the combustion of organic hydrogen compounds in oxygen, molecules of water, of hydroxyl (OH), of carbon (C_2) and of carbon monoxide, are present. These molecules also exist in electrical discharges which pass through organic vapors, provided these contain the elements oxygen and hydrogen as constituents. In flames an excess of oxygen converts the carbon partly into carbon dioxide. In electrical discharges in pure organic vapors such an excess of oxygen is not present, so that practically no carbon dioxide is formed, and oxygen and carbon are combined almost entirely as carbon monoxide. Carbon is present as molecules of C_2, of CH, and as carbon atoms and singly charged positive carbon ions (C^+), while hydrogen is found also as atoms (H).

Such atoms, ions and molecules are obviously extremely active, and unite rapidly to form very complex organic liquids or solids. For example, Lind and Glockler[1] found that silent, semi-corona and corona discharges effect the condensation, with a liberation of hydrogen and some methane, of the lower saturated hydrocarbons and of ethylene. With the ozonizer type of discharge, the products are almost entirely liquid, whereas the corona type of discharge yields as much resinous solid as liquid product. Similarly, Lind and Bardwell[2] found that a-radiation causes the condensation of the lower saturated hydrocarbons with elimination of hydrogen and methane and the formation of higher saturated and unsaturated hydrocarbons, which may be gaseous, liquid or solid. Carbon monoxide gives carbon, carbon dioxide and a solid, presumably a suboxide of carbon. With unsaturated compounds, Lind, Bardwell and Perry[3] obtained solid polymers from acetylene, cyanogen and hydrogen cyanide under the influence of a-particles, and a colorless liquid condensate from ethylene upon elimination of one-sixth of its content of hydrogen.

The effect of canal rays was studied as early as 1906 by Kinoshita,[3a] who worked with several gases, including acetylene, and obtained characteristic line and band spectra. More recently, Kohlschiitter and Frumkin[3b] investigated the decomposition of hydrocarbons by canal rays.

The electrodeless discharge, as the writers have reported,[4] is a convenient means of effecting the polymerization or condensation of organic compounds. Thus, when benzene vapor at a pressure of 0.1 mm. (relatively low compared to the pressures used by Lind and his co-workers) is subjected to the electrodeless discharge, a greenish-white, ring-like glow appears, concentric with and adjacent to the coil of wire which supports the discharge. This glow immediately spreads through the entire flask, and is extinguished in a red flash, since the benzene is converted into a solid, so that the pressure falls too low to carry the discharge. If, how-

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Lind and Glockler, THIS JOURNAL, 50,1767 (1928); 51,2811,3655 (1929).

[2] Lind and Bardwell, *ibid.*, 47,2675 (1925); 48,2335 (1926).

[3] Lind, Bardwell and Perry, *ibid.*, 48, 1556 (1926).

[3a] Kinoshita, *Physik. Z.*, **8**, 35 (1907).

[3b] Kohlschütter and Frumkin, Ber., **54B**, 587 (1921).

[4] Harkins and Gans, THIS JOURNAL, 52,2578 (1930).

ever, benzene vapor is continuously admitted at the proper pressure, the discharge persists as a brilliant white ball, arid a brown solid deposits on the walls of the vessel. The formula of this product is (CH),. The spectrum from the discharge shows that the benzene is first decomposed into neutral hydrogen (H) and carbon (C) atoms, into singly charged carbon ions (C^+), and into molecules of carbon (C_2) and monohydrocarbon (CH).[5]

Other organic substances form similar compounds and give related spectra. If oxygen is present in the substances, molecules of water, of hydroxyl (OH) and of carbon monoxide are formed as intermediate products, as has already been stated. If nitrogen, but not oxygen, is present, cyanogen (CN), nitrogen (N_2), singly charged N_2^+ ions and imine (NH) molecules are formed.

In general, these atoms, molecules and ions react with each other very rapidly, almost instantaneously, to form products of higher molecular weight. For example, benzene is decomposed and the fragments unite to form a reddish-brown solid almost as rapidly as the benzene vapor can flow into the flask at the proper reduced pressure. One exception is the product water, which is relatively inactive and does not seem to unite to any very great extent with the other materials produced by the decompositions.

2. Apparatus and Procedure

The apparatus used in these experiments is shown in Fig. 1. Here F is a 1-liter pyrex flask which contains the vapor studied. Over the mouth of the flask, a quartz window Q is attached with de Khotinsky cement. The tube E, sealed to the neck of the flask, acts as a trap for any solid product which may be thrown against the window, and, when necessary, as a liquid-air trap. Around the flask, in the plane passing through the

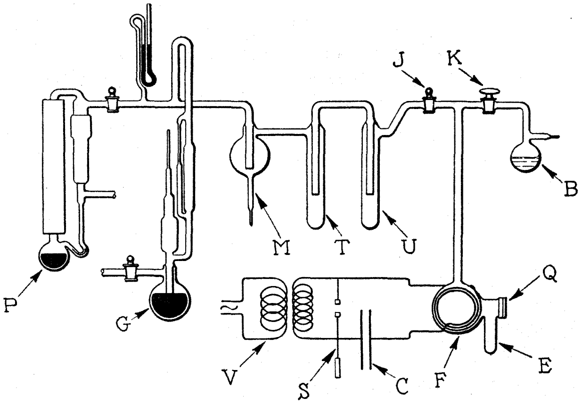

Fig. 1.

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[5] This is confirmed by Austin, This journal, 52, 3026 *(1930).*

window, is tightly wound a vertical coil of six turns of insulated, heavy copper wire. In addition to this coil, the high-frequency circuit consists of a 1 kv. a. Thordarson transformer V which supplies 25,000 volts, a spark gap S capable of adjustment by a screw and made of cylindrical zinc electrodes 1.7 cm. in diameter, and a 0.02 microfarad condenser C of 14 squares of sheet metal immersed in transformer oil between plates of double-strength window glass in a metal container. The frequency of the circuit, as determined with a radio receiver, was about 1100 kilocycles per second.

Vapor is admitted to the flask F from the supply bulb B. Mercury vapor from the diffusion pump P, which is backed up by a Cenco Hyvac pump, is kept from the flask by the liquid-air trap T, while the liquid-air trap U prevents the substance in the bulb from getting into the pumps. The special McLeod gage G is capable of measuring pressures up to several millimeters of mercury.

The compound to be studied, properly purified and dried, is distilled into the bulb B, which is then sealed, except for the outlet through stopcock K. After the air is pumped out of the bulb, stopcock K is closed and the apparatus is completely evacuated. Stopcock J is now closed permanently, the electrodeless discharge is started and vapor is admitted to the flask F through stopcock K. The vapor, as it enters the vessel, is decomposed with emission of light and formation of the products already mentioned.

The discharge is very sensitive to pressure changes and operates at low pressures. With a very volatile liquid, the stopcock K must therefore be opened only very slightly, and it is sometimes necessary to surround the bulb B with a properly chosen cooling agent. The vapor pressure of a relatively non-volatile solid or liquid may not be high enough at room temperatures to support the discharge, in which case that part of the apparatus which lies to the right of stopcock J is enclosed in a box which contains an electrical heater capable of maintaining the contents of the box at 60° or more. When the pressure in the flask F is correctly controlled, the decomposition can be continued without interruption for several hours. Should the compound form products whose vapor pressure is too high at ordinary temperatures, the side-arm E is surrounded with liquid air. The discharge causes a considerable evolution of heat, which is dissipated by the use of a fan.

The light which passes out through the window Q is focused on the slit of a spectrograph. In this work a Hilger E1 quartz spectrograph and a Steinheil GH glass spectrograph were used. A small plane silver mirror, placed when desired at an angle of 45° just in front of the quartz window, throws the spectrum of an ion arc on each plate, for comparison. For work in the visible region, panchromatic plates were used. The deposition of a firmly adhering film of product necessitated a change of window after each exposure, which lasted from one-half to two hours.

3. Purification of Compounds

The compounds studied were benzene, acetylene, naphthalene, n-heptane, aniline, nitrobenzene, phenol and chlorobenzene. Acetylene was prepared[6] by dropping ethylene dibromide into 30% alcoholic potash at its boiling point. To remove vinyl bromide the gases evolved were passed through a series of two coil condensers, through which ice-water was circulated. The acetylene was collected over water, passed over phosphorus pentoxide and repeatedly through a trap surrounded by carbon dioxide snow to remove water and any remaining vinyl bromide. The acetylene was finally isolated in the bulb B over liquid air. C. P. naphthalene was used. With the other compounds, the middle fractions obtained by distillation of the C. P. reagents were dried over sodium,

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[6] This procedure was suggested to us as the best method for preparing pure acetylene by Prof. M. S. Kharasch.

phosphorus pentoxide, or anhydrous sodium sulfate, and distilled into the bulb B under reduced pressure.

4. Effects of the Electrical Discharge

(a) Benzene.—-With benzene, no liquid air was required around the side tube E. In half an hour several thousand liters of vapor were admitted continuously to the discharge vessel, and decomposed, yet not enough permanent gas accumulated in the flask to extinguish the discharge, despite its sensitivity to pressure changes. This is evidence that the fragments produced by decomposition reunite completely to form the reddish-brown solid observed. Analysis of the product gave $(C_{1.00}H_{1.00})_n$ as its average composition. It was insoluble in ordinary solvents, although a continuous extraction with xylene in a Soxhlet apparatus for three weeks yielded a brown solution which left a small amount of gummy, viscous liquid on evaporation of most of the solvent. On further heating the product charred before the xylene was completely removed. No fraction could be pumped off from the solid in *vacuo,* although it was heated above **100°** and liquid air was used as the condensing medium. A sample of the solid gained **1.0%** in weight after being exposed to the atmosphere for twenty days, and 2.5% after sixty-six days, through absorption of oxygen, adsorption of water vapor, or both.

Benzene vapor at a pressure of **0.25 mm.** of mercury could be decomposed by the discharge only when the spark gap was increased to 6 mm. At lower pressures, not so long a spark gap was required. Thus, at a pressure of **0.14** mm., a spark gap of **3** mm. sufficed, while at 0.03 mm. pressure, a spark length of 1.5 mm. effected decomposition. At a pressure of about **0.1 mm.,** approximately **1.2** g. of solid was produced per hour.

These data are summarized in Table I. The first column gives the color of the initial ring discharge, greenish-white in the case of benzene. In the second column is the color of the brilliant glow within the flask when decomposition is in progress. This glow completely fills the flask at intermediate pressures, but shows a non-luminous core at higher pressures. It was this glow, white for benzene, which was photographed. The next column of Table I gives the color of the product. The solid formed on the walls, and peeled off as a powder, as thin flakes or as thick scales, depending on the substance decomposed. The physical form of the product is listed in the fourth column. That part of the solid which did not peel off clung tenaciously to the glass, but could be cleaned away by filling the flask with water, which seemed to get between the glass and the film with great ease. **A** fresh, dry flask was used for each substance. In the last column is given the approximate rate of formation of the product in grams per hour at an intermediate pressure. Data for all the substances studied are presented in Table I.

TABLE I

Substance	Color of discharge Ring	Glow	Color of product	Form of product	Rate of formation of product, *g.* per hour
Benzene	Greenish-white	White	Medium brown	Powder and small scales	1.2
Acetylene	Bluish-white	White	Medium brown	Powder and small scales	1.3
Naphthalene	Violet-white	White	Very dark brown	Thick scales	1.2
n-Heptane	Bluish-white	Reddish-white	Yellow brown	Very thin scales	0.00
Aniline	Violet-white	Bluish-white with red spots	Medium brown	Powder and scales	0.9
Nitrobenzene	Bluish-white	White	Dark brown	Thick scales	0.7
Phenol	Violet-white	White with red spots and greenish-blue center	Medium brown	Powder and scales	0.4
Chlorobenzene	Greenish-white	Greenish-white with red at center	Black	Powder and thick scales	0.4

Photographs of the decomposition spectrum for benzene are shown in Figs. 2 and 3. The fainter portions, easily visible in the original plates, are here indiscernible, because of repeated reproduction. The spectrum taken with the Steinheil instrument, Fig. 2, extends from 6600 to 3800 Å., and that taken with the Hilger spectrograph in the first position, Fig. 3a, from 6600 to 3300 Å. Spectrograms were also secured with the Hilger instrument in the second position, which carried the work down to 2400 Å. in the ultraviolet.

The decomposition spectrum of benzene showed all five groups of Swan bands very prominently. The other C_2 bands, discovered by Deslandres and D'Azambuja[7] and analyzed and discussed by Dieke[8] and by Johnson[9] were also present, though faintly, at λ4102, λ4068, λ4041, λ3852, λ3826, λ3607, λ3593, λ3588, λ3400 and λ3398. The CH bands at λ4300 and λ3900 were both prominent, and the first five lines of the Balmer series of hydrogen, H_α to H,, were very apparent. The line spectrum of C^+ and the line due to C at λ2478 were also present. The relative intensities are tabulated in Table II, which lists similar data for all of the compounds investigated.

When the decomposition was carried out at the lowest possible pressures, the nature of the spectrum was changed. The glow itself became

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[7] Kayser, "Handbuch der Spektroskopie," Vol. V, **234.**

[8] Dieke, ***Nature,*** 125, **51** (1930).

[9] Johnson, *ibid.,* 125, 89 (1930).

TABLE II

RELATIVE INTENSITIES

	Substance							
	Benzene	Acetylene	Naphthalene	n-Heptane	Aniline	Nitrobenzene	Phenol	Chlorobenzene
Exposure, hrs....	0.5	0.75	0.5	0.5	1	2	1.5	1
Intermediate decomposition product								
CH	4	3	2	2	3–4	2	3	
Swan C_2	5	4	4		4	3	3	1
C_2[a]	2	2			1	1	2	
C^+ (C)	3	2	2	1	3	3	3-4	1
H	4	4	3	5	3	3	3	3
CN					5	5		
NH					2–3			
N_2					2	2		
N_2^+					2	2		
CO						2	1	
OH						3	3	
Cl								5

[a] C_2 bands other than Swan bands.

1, Very weak; 2, weak; 3, average; 4, intense; 5, very intense.

much redder and weaker and what bands appeared were very feeble in intensity. The Balmer series for hydrogen became relatively more prominent, and, despite the precautions taken to keep mercury vapor out of the discharge vessel, there appeared an intense line spectrum of mercury corresponding to that excited by the spark, rather than the arc.

The spectrum thus indicated the intermediate existence of C^+ ions, C and H atoms and CH and C_2 molecules during the decomposition of the benzene.

(b) Acetylene.—The product obtained with acetylene resembled that for benzene. To cool the side tube E was not necessary. The spectrum was the same as for benzene. The details are given in Tables I and II.

(c) Naphthalene.—Naphthalene produced a very dark brown product, which flaked off the glass in thick scales. No liquid air was required around tube E. The initial electromagnetic ring discharge did not show as great a tendency as with benzene to spread through the flask to give decomposition. The decomposition spectrum differed from that for benzene in its lower intensity for the same time of exposure.

(d) *n*-Heptane.—*n*-Heptane reacts differently from the unsaturated hydrocarbons. Although an amber-colored solid was formed on the walls, the quantity was very slight. When the discharge vessel was filled with n-heptane vapor at the proper pressure and stopcock K was closed, the pressure on decomposition seemed to rise slightly, rather than to fall. If fresh vapor was admitted to the flask, the discharge was extinguished because of the increase in pressure. Nor was the passage of the discharge made possible when the side tube E was immersed in liquid air, if vapor was continuously admitted to the flask. No liquid products were visible. The gaseous products could not be condensed with liquid air. The spectrum consisted of the Balmer series, which was very prominent, of the CH bands, which were faint, and of the C line at λ2478. In addition, an intense mercury spectrum was present, as it was for benzene when decomposed at the lowest pressures.

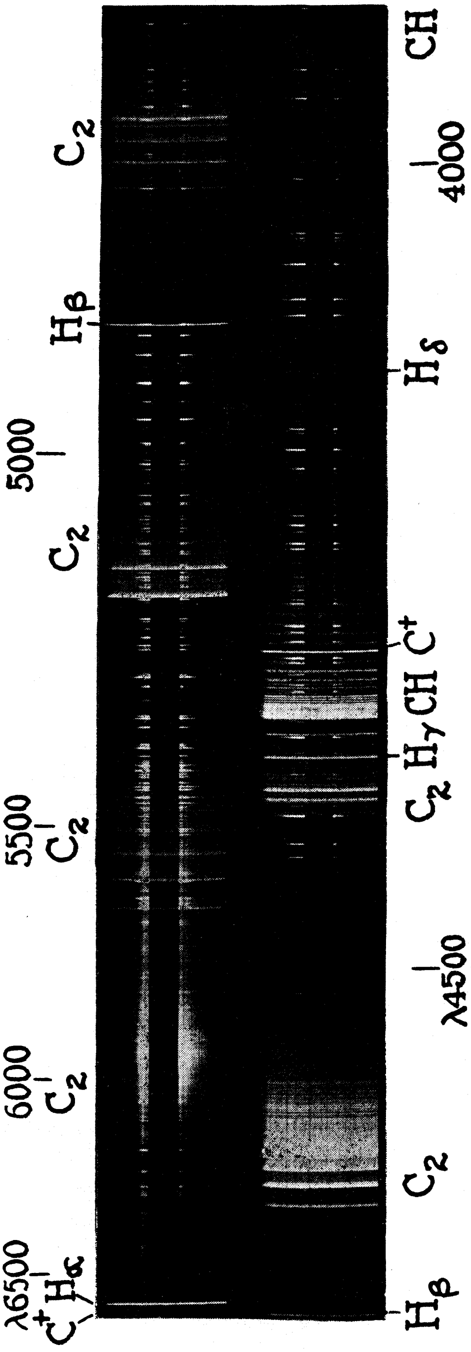

Fig. 2.—Spectrum obtained when benzene is decomposed in the electrodeless discharge. Taken with a Steinheil GH glass spectrograph. The spectrum of the iron arc is also shown.

(e) Aniline.—With aniline, it was necessary to immerse the side tube E in liquid air in order to keep the pressure low enough for the discharge to pass. The product had a strong odor of bivalent carbon compounds, which made difficult the detection by smell of ammonia and the lower amines, but neutral litmus paper, when inserted into a freshly opened flask F, rapidly turned blue.

In the spectrum, the violet cyanogen bands were prominent, from Group II at λ4532 to Group V at λ3590. The β-bands of NH, at λ3360 and λ3370, were visible. The second positive group of N_2 appeared at λ3577, λ3371 and λ3159, and the first negative group, due to N_2^+, showed at λ3914. The spectrum characteristic of benzene was also present, although subdued. The spectrogram obtained for aniline with the Hilger spectrograph in its first position is reproduced in Fig. 3b, next to that for benzene.

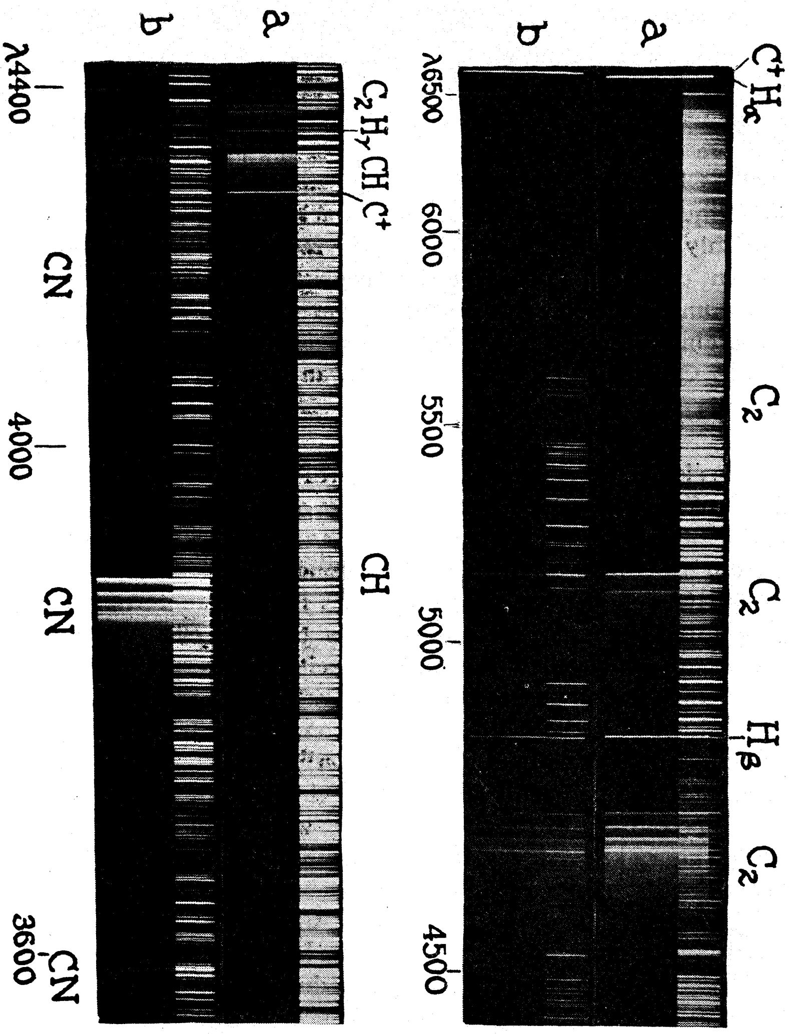

Fig. 3.—(a) Spectrum given by benzene when decomposed in the electrodeless discharge. Taken with a Hilger El quartz spectrograph. The narrow spectrum is that of the iron arc. (b) Spectrum obtained with aniline, showing cyanogen bands not found with benzene.

(f) Nitrobenzene.—For continuous decomposition, nitrobenzene required liquid air at E. The product did not have the strong odor of the solid from aniline, and was dark and coarse, although *a* slight deposit that formed at the neck of the tube E was much lighter in color, a characteristic that was observed also with other compounds. Moist neutral litmus paper was not affected when it was held in a flask F opened just after the end of an exposure. The spectrum was in general like that for aniline, but showed also the OH band at λ3064 and the CO bands at λ2974 and λ2832, as for phenol. A search for NO bands was made down to λ2200, but none was found after a two-hour exposure.

(g) Phenol.—To condense the water vapor which phenol forms on decomposition, liquid air was kept around the tube E. In addition to the typical benzene decomposition spectrum, phenol showed the water vapor band, for which the carrier is OH, at λ3064, and, faintly, the third positive group of carbon, due to CO, at λ2974 and λ2832.

(h) **Chlorobenzene.**—With chlorobenzene, also, the tube E was cooled with liquid air. The product was black, and neutral litmus thrust into a freshly opened flask quickly turned red, indicating the presence of hydrogen chloride. The spectrum consisted almost entirely of the line spectrum of chlorine, as excited by the spark, but the first three lines of the Balmer series for hydrogen were present. Also, some of the lines due to C^+ and C and part of the Swan bands were very faintly visible.

4. Discussion

The electronic energy utilized in breaking up the molecules is in part given off as radiation, and the energy of this radiation gives some idea of the range of the electronic energy and velocity involved. This range is from 1.8 to 5 volts, which corresponds to velocities from 8×10^7 to 1.3×10^8 cm. per sec. and to energies from 41 to 115 kg. cal. per mole. Undoubtedly electron velocities below this are effective in breaking up the organic molecules, but such velocities correspond to the infra red spectrum, which has not been investigated. According to Hittorf[10] and J. J. Thomson[11] the electrodeless discharge is due to electromagnetic induction, but Townsend and Donaldson[12] consider it to be caused by the electrostatic potential. MacKinnon[13] has shown that Thomson's work has been confined to the ring discharge, which is electromagnetic in origin, while the relatively weaker glow discharge investigated by Townsend and Donaldson is electrostatic. In the present work both types of discharge existed, but the decomposition always started as a ring discharge.

It may be assumed that the decomposition of the organic vapors into simpler molecules, atoms and ions is due to free electrons. These gain velocity, due to the field, between impacts. The higher the pressure of the gas, the smaller the mean free path of these electrons, and the more rapidly must the electrons gain velocity in order to attain any definite final velocity at the time of impact with a molecule. For this reason

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[10] Hittorf, *Wied. Ann.*, 52, 473 (1884).

[11] J. J. Thomson, *Phil. Mag.*, [7] **4**, 1128 (1927); [5] 32, 321, 445 (1891).

[12] Townsend and Donaldson, *ibid.*, [7] 5, 178 (1928).

[13] MacKinnon, *ibid.*, [7] **8**, 605 (1929).

it is necessary to increase the voltage on the coil as the pressure of the gas increases, if the discharge is to continue to pass. Since there are great differences in the individual electron mean free paths as well as differences between the electrostatic and the electromagnetic fields, the individual electrons attain very different velocities before impact. If the velocities are in general too small, the discharge will not pass through the gas, since not enough ions and free electrons are produced.

It is not the intention of the preceding paragraph to indicate that the effects of ions, produced by electron bombardment, in causing ionization and dissociation by collisions of the second kind are negligible. There may be, in addition, some dissociations produced by collisions of the first kind, other than those due to electrons.

The writers wish to thank the National Research Council for a grant which has enabled them to secure a Steinheil GH glass spectrograph for use in this and other spectroscopic work.

5. Summary

1. In the electrodeless discharge organic vapors are commonly decomposed into simpler molecules, atoms, ions and electrons. For example, benzene is rapidly decomposed into molecules of monohydrocarbon (CH) and of carbon (C_2), into atoms of carbon (C) and of hydrogen (H), and into singly charged positive ions of carbon (C^+). Phenol gives all of these products and molecules of hydroxyl (OH), of water (H_2O) and of carbon monoxide (CO) in addition. Aniline gives the same decomposition products as benzene, and also single molecules of cyanogen (CN), of imine (NH), of nitrogen (N_2) and singly charged molecular nitrogen ions (N_2^+). Acetylene and naphthalene give the same products as benzene.

2. The intermediate decomposition products listed in (1) are extremely active and unite very rapidly to form brown or black solids which are insoluble in water and organic liquids, and which doubtless have high molecular weights.

3. n-Heptane, unlike the unsaturated hydrocarbons, gives very little solid in the type of apparatus here employed. During the decomposition of this saturated compound there exists much atomic hydrogen (H), relatively few molecules of monohydrocarbon (CH) and some neutral atoms of carbon (C).

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE MOLECULAR WEIGHT OF EGG ALBUMIN. II. IN THE PRESENCE OF ELECTROLYTES[1,2]

BY J. B. NICHOLS

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The investigation of the molecular weight of egg albumin in salt-containing solutions to be reported in this paper is a continuation of the ultracentrifugal study of egg albumin described in 1926.[3] The experimental data were obtained in 1927, but certain points arose which were difficult to explain and which were thought to be due either to experimental error or to abnormalities in the behavior of the protein. The data were therefore set aside to await confirmation.

Although the sedimentation-equilibrium method had given very concordant results and had indicated that egg albumin was composed entirely of molecules 34,500 in weight the diffusion constant from the sedimentation-velocity runs, even in electrolyte-free solution, was only about six-tenths of the required value calculated from the molecular weight and the sedimentation velocity and was fairly irregular from run to run. On the other hand, the specific sedimentation velocity gave reasonable values throughout.

At first it was thought that a slight temperature inequality was present leading to a small convection current which made the diffusion constant appear smaller than it actually was but had no marked effect on the sedimentation velocity.[4] However, a more detailed study of other abnormal cases that have since appeared suggests that the egg albumin centrifugings were not in error and that the material had not undergone harmful decomposition. In a recent paper on Bence-Jones[5] protein a discussion has been given of these abnormalities in the diffusion constant. Since then more examples of abnormal diffusion have been met with. For many of the proteins thus far studied, the values of molecular weights obtained from the sedimentation-equilibrium and the sedimentation-velocity methods have agreed within the experimental error. This fact signifies that the molar frictional coefficient active in free diffusion is often the same as that effective in sedimentation—especially at the isoelectric point. However, hemo-

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[1] Presented at the Minneapolis (September, 1929) meeting of the American Chemical Society.

[2] The author wishes to acknowledge the aid given him by E. I. du Pont de Nemours & Company, which rendered possible the completion of this work.

[3] Svedberg and Nichols, THIS JOURNAL, **48**, 3081 (1926).

[4] Cf. Rinde, "The Distribution of the Sizes of Particles in Gold Sols," Dissertation, Upsala, 1928, pp. 85–87.

[5] Svedberg and Sjögren, THIS JOURNAL, **51**, 3594 (1929).

cyanin[6] and cuprammonium cellulose[7] have shown abnormalities due to hindered diffusion in the more concentrated solutions, the first on account of its large size and the second probably because of its thread-like nature. This hindrance to diffusion caused by the too close proximity of the molecules in the more concentrated solutions disappears in sufficiently dilute systems. The same explanation does not suffice for egg albumin, Bence-Jones protein and some other proteins because the molecules are small! compared with hemocyanin and regular compared with cuprammonium cellulose. Further consideration must be given to this problem before it will be possible to state with certainty what the cause is of the abnormally small diffusion of the proteins with small molecules.

On the other hand, the sedimentation velocity behaved normally for egg albumin and gave consistent results under conditions which have been found to produce normal behavior in other proteins: (1) sufficiently salt-free, stable solutions as prepared by electrodialysis; (2) well-buffered solutions in the neighborhood of the isoelectric point; **(3)** solutions containing buffering or neutral salts in quantity insufficient to cause "salting-out." Therefore only determinations of the sedimentation constant will be used to characterize the egg albumin in different ionic environments, but it is well to mention in passing that the value found for the diffusion constant of egg albumin at 30° is roughly 0.065 sq. cm./day or 0.076 $\times 10^{-5}$ sq. cm./sec., which is of the same order as Herzog's value? 0.087 $\times 10^{-5}$ sq. cm./sec. when the latter is adjusted to the same temperature, 30°.

Experimental

The egg albumin used in the experiments was crystallized according to the method of Sørensen,[9] and dialyzed for fifteen days in flowing distilled water at 0°, saturated with toluene. The material was further purified previous to the experiments by electrodialysis at a current density of *0.3* ma./sq. cm., bringing down the conductivity of a 1% solution to *1.3* X 10^{-5} mhos at 18°. The solutions were brought to the desired concentration and salt content or PH immediately before starting the centrifuge runs. In the neighborhood of the isoelectric point the partial specific volume was taken as *0.754* at 30° except in sodium chloride solutions, where $V = 0.749$.[10] The reason for this depressing action is not clear Sodium chloride would be expected to show a dehydration effect but it is not evident that such an effect would produce the observed depression of the value of the partial specific volume.

Table I shows that the partial specific volume does not vary over an appreciable PH range, in fact not until we reach strongly acid solutions.

All of the experiments were carried out in the high-speed oil-turbine type

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[6] Svedberg and Chirnoagă, THIS JOURNAL, *50, 1401 (1928).*

[7] Stamm, *ibid., 52,3047 (1930).*

[8] Herzog, *Z. Elektrochem.,* 13, *539 (1907).*

[9] Sørensen, *Medd. Carlsberg* Lab., 12, 12 *(1917).*

[10] The value of *0.749* for egg albumin solutions containing sodium chloride has also been obtained at the du Pont Experimental Station.

TABLE I

VARIATION OF PARTIAL SPECIFIC VOLUME IN DIFFERENT SOLVENTS AT 30°

Solvent	P_{H} of soln.	Partial sp. vol
0.102 *N* HCl	1.16	0.759
0.010 N HCl	2.44	..
Acetate buffer 0.025 N with respect to sodium	3.6	.755[a]
0.02 *N* acetate buffer	4.7	.754
1.0% NaCl solution	4.75	.749
Electrolyte-free	4.67	.754[a]
Acetate buffer 0.025 *N* with respect to sodium	5.4	.754[a]
0.017 M primary–secondary phosphate buffer	7.3	.749

[a] These values are adjusted to 30° from a temperature of 19.2°.

of ultracentrifuge[11] with the exception of the one sedimentation-equilibrium experiment. As shown in previous communications the molecular weight is determined from the sedimentation equilibrium [3,12] by the relation

$$M = \frac{2\,RT \ln (c_2/c_1)}{(1 - V\rho)\,\omega^2\,(x_2 + x_1)(x_2 - x_1)} \qquad (1)$$

and from the sedimentation velocity[10,13] by the expression*

$$M = \frac{RT\,s}{(1 - V\rho)D} \qquad (2)$$

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 velocity, c_2 and c_1 the concentrations at the distances x_2 and x_1 from the center of rotation, D the diffusion constant and $s = (\mathrm{d}x/\mathrm{d}t)\ (1/\omega^2 x)$, the specific sedimentation velocity or sedimentation constant.

Since, however, the diffusion constant for egg albumin is abnormal, Equation 2 is not valid as it stands, and the results will be left in terms of s, the sedimentation constant, which will be shown later to be equal to the value calculated from the molecular weight determined by sedimentation-equilibrium measurements.

The solutions were subjected to a centrifugal force approximately 100,000 times that of gravity. Exposure time was from twenty to forty seconds and the usual time of centrifuging was three to four hours. Pictures of the sedimenting system were taken every half hour. The length of column of solution used was from 13 to 15 mm. and the thickness 2 mm. All values refer to 1% egg albumin at 30°. The absorption band of egg albumin in the short ultraviolet region of the spectrum was employed in making the concentration determination in the centrifuge by isolating the wave length range 290–240 mμ from the mercury arc by means of gaseous chlorine and bromine filters. Imperial Process plates were used on account of their

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[11] Svedberg and Nichols, THIS JOURNAL, 49, 2929 (1927).

[12] Svedberg and Fåhraeus, *ibid.*, 48,430 (1926).

[13] Svedberg and Lysholm, *Nova Acta Reg. Soc. Scient. Upsaliensis*, Vol. ex. ord., ed. 1927.

thin, uniform emulsion and were developed with Eclipse metol-hydroquinone developer.

Figure 1 gives a reproduction of the photographic record of the centrifuging of an acetate buffer solution of 1.0% egg albumin at a PH of 4.7. This experiment was performed at 30° and at a speed of 41,900 r. p. m. corresponding to a centrifugal force of nearly 100,000 times that of gravity. The first exposure to the left shows the condition of the solution at the start of the run, and succeeding exposures show it after one-half, one hour, etc., up to three and one-half hours of centrifuging.

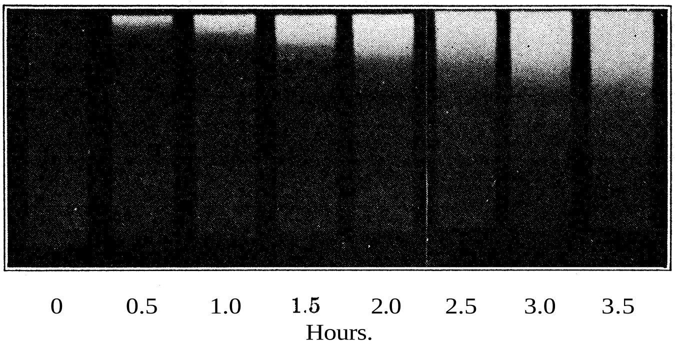

Fig. 1.—Sedimentation of egg albumin at 4.7 PH.

Table II contains typical data describing a centrifuge run. It refers to a 1.0% solution of egg albumin 0.0102 N with respect to hydrochloric acid and gives results from one of the three plates used in calculating the s-value for this solution.

TABLE II

SPECIFIC SEDIMENTATION VELOCITY OF EGG ALBUMIN IN 0.01 N HYDROCHLORIC ACID

Egg albumin concn., 1 g. per 100 cc.; HCl concn., 0.0102 N; PH of solution, 2.44; T, 303.1°K; length of column, 1.39 cm.; thickness of column, 0.20 cm.; Imperial Process plates; short ultraviolet illumination (290–240 mμ region isolated from the mercury arc by gaseous chlorine and bromine filters); exposure time, 20 sec.; Eclipse metol-hydroquinone developer, 2 min.

Time interval, hr.	Δx, cm.	$x_{\text{med.}}$, cm.	Speed, r. p. m.	Centrifugal force $\omega^2 x$	Sp. sedimentation velocity, $s_{30°}$ cm./sec.
0.5–1.0	0.044	4.625	41,880	8.90×10^7	2.81×10^{-13}
1.0–1.5	.048	4.671	41,780	8.94	2.98
1.5–2.0	.044	4.717	41,650	8.98	2.69
2.0–2.5	.046	4.762	41,380	8.94	2.81
2.5–3.0	.048	4.809	41,370	9.03	2.89
3.0–4.0	.102	4.884	41,280	9.13	3.03
				Mean s =	2.87×10^{-13}

Table III gives the values for the sedimentation constant obtained in the isoelectric region of the protein. In common with the findings on the majority of the proteins thus far studied, the addition of salts or buffer solutions of the same P_H as the isoelectric point of the protein does not affect the molecular condition of the protein, as evidenced by the constancy of the sedimentation velocity. Furthermore, the mean value obtained for the sedimentation constant, 4.06 × 10^{-13} cm./sec., is nearly the same as the s-value for Bence-Jones protein.[14] Reduced to the same temperature, 20°, the sedimentation constant of egg albumin is 3.25 × 10^{-13} cm./sec., while that for Bence-Jones protein is 3.55 × 10^{-13} cm./sec.

TABLE III

SEDIMENTATION VELOCITY OF ISOELECTRIC AND OF SALT-FREE EGG ALBUMIN

Solvent	P_H of soln.	Speed, r. p. m.	Mean centrifugal force	Sp. sedimentation velocity, $s_{20°}$ in cm./sec.
Water	4.67	41,800	9.61 × 10^7	4.03 × 10^{-13}
Water	4.67	41,430	9.04	3.94
0.02 *N* acetate buffer	4.70	41,370	9.63	4.07
0.017 *N* acetate buffer	4.70	41,900	9.16	4.12
0.7% NaCl	4.73	41,290	9.12	4.15
			Mean s =	4.06 × 10^{-13}

By the sedimentation-equilibrium method both proteins have been found to possess a molecular weight of approximately 34,500. Using the s- and M-values determined, respectively, by the sedimentation-velocity method and by the sedimentation-equilibrium, we may determine whether these proteins consist of spherical molecules.[5] The molar frictional constant calculated from the sedimentation velocity was found to agree closely with that calculated for a substance of molecular weight 35,000 and possessing spherical molecules of the same specific volume as the two proteins. As mentioned in the article cited, the radius of the egg abumin molecule is 2.17 mμ as compared with 2.18 mμ for Bence-Jones protein.

In a recent paper on the osmotic pressure of egg albumin, Marrack and Hewitt[15] determined the molecular weight of egg albumin to be 43,000 in salt solutions as compared with the present determination of 34,500 both in salt-containing and in salt-free solution. Unpublished data tend to support their consideration that a small amount of impurity in constant amount might be formed in salt-containing solutions on standing. This small amount of material is perhaps the first step in the slight precipitation of denatured egg albumin that always occurs on standing. An electrodialyzed, salt-free solution of egg albumin is relatively stable. In the high-speed type of ultracentrifuge the whole experiment is completed in three or four hours after the addition of the salt or buffer, so there is much less chance for the formation of the approximately 5% of aggregated material required to give the average value of 43,000 found by the osmotic method that requires from one to two days to reach equilibrium. Under

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[14] Svedberg and Sjogren, Ref. 4, p. 3603.

[15] Marrack and Hewitt, *Biochem. J.*, 23, 1082 (1929).

conditions comparable to the osmotic method, however (*e. g.*, in the sedimentation-equilibrium method at ordinary temperatures, which requires two days of centrifuging), a change in the egg albumin frequently occurs, causing an increase in light absorption and the appearance of a small amount of aggregated material at room temperature.

As the isoelectric region is left, the sedimentation velocity seems to be decreased slightly more than the experimental error would account for.

TABLE IV

DEPRESSING EFFECT ON THE SEDIMENTATION CONSTANT IN ACID AND ALKALINE EGG ALBUMIN

Solvent	PH of solution	Sp. sediment. velocity s in cm./sec.	s/s_0
0.34 *N* acetate buffer	3.53	3.59×10^{-13}	0.89
0.017 M double phosphate buffer	7.4	3.57×10^{-13}	.885

Table IV shows the possible slight depressing effect occurring in an egg albumin solution buffered at a PH of 3.53 with 0.34 N acetate buffer and in a solution buffered at a PH of 7.4 with 0.017 M primary-secondary phosphate buffer. The normal sedimentation velocity, s_0, has been reduced by nearly the same ratio, respectively, 0.89 and 0.885, in each case.

Table V gives evidence from the sedimentation equilibrum of 3.59 PH egg albumin in 0.2 *N* acetate buffer, that the possible slight depression of the s-value in moderately acid egg albumin is not due to a slight Donnan effect since the buffer concentration is actually lower for the sedimentation-equilibrium run than for the sedimentation-velocity run. The value for the molecular weight is normal; therefore, it follows that the depression of the s-value did not arise from an electrical effect produced by a partial separation of charges in the centrifuge.

TABLE V

SEDIMENTATION EQUILIBRIUM OF 3.59 PH EGG ALBUMIN IN 0.2 *N* ACETATE BUFFER

Concentration, 0.97 g./100 cc.; speed, 10,900 r. p. m. ($\omega = 363.3$~;) mean centrifugal force, 5.84×10^6 dynes; length of column, 0.53 cm.; V = 0.749 at 18°; T = 291°; density of solution, 1.0019; exposure times 29, 36.5, 41.5 hours after the start; lengths of exposure, 20, 40, 80 and 160 seconds; Imperial Eclipse Plates, metol developer, 3 minutes' development

Distances, x_2	Cm. x_1	Mean concn. % c_2	c_1	Number of exposures	M
4.68	4.63	1.555	1.397	8	34,800
4.63	4.58	1.397	1.266	7	32,200
4.58	4.53	1.266	1.144	7	33,750
4.53	4.48	1.144	1.041	9	31,600
4.48	4.43	1.041	0.943	7	33,500
4.43	4.38	0.943	.849	8	35,750
4.38	4.33	.849	.772	8	33,100
4.33	4.28	.772	.701	8	33,950
4.28	4.23	.701	.635	7	35,000
				Mean	33.740

Repression of Donnan Effect.—If we add acid or alkali to a salt-free protein and subject the solution to a high centrifugal force, a partial separation is produced of the large protein ion from the small inorganic ions of opposite sign. An electrical potential acting in opposition to the centrifugal potential is thereby set up similar in character to the Donnan membrane potential. In the simplest case—no foreign ions present—which we very likely approximate for unbuffered solutions, the effect of the electrical potential is to reduce the true value of the molecular weight by the factor[16] $(n + 1)$ or

$$M = \frac{(n+1)RT\,s}{(1-V\rho)\,D}$$

where n is the mean valence of the protein ion. Thus it is possible to gain some information about the mean valence of a protein by first centrifuging in unbuffered acid or alkaline solution and then centrifuging another sample to which has been added sufficient electrolyte to repress the electrical potential to a negligible value. The latter determination is made chiefly for the purpose of showing that no actual change has occurred in the molecular weight at the given P_H value.

In order to give some idea of the action of the Donnan effect on the diffusion constant as well as on the sedimentation constant, the values of D as well as those of *s* are given in Table VI. It is evident that the electrical effect produced by the separation of the ions has a much greater effect on the diffusion constant than it has on the sedimentation constant. The values of D given in the table should be considered only apparent as mentioned earlier, but they at least illustrate the action of the Donnan effect. No attempt has been made to calculate the valence of the protein ion from the changes produced in the D and the s-values by the free acid or alkali because relatively minute quantities of decomposition products largely repress the true Donnan effect. For the 0.01 N HCl solution, the amount of free acid present amounts to approximately 36% of that added, thus

TABLE VI

REPRESSION OF DONNAN EFFECT

Expt.	Solvent	P_H of solution	Apparent diffusion constant, $D_{30°}$, sq. cm. /day	Sedimentation constant, $s_{30°}$ cm./sec.
1	0.001 N HCl	3.94	0.111	3.19×10^{-13}
2	0.34 N acetate buffer	3.53	.061	3.59[a]
3	0.01 N HCl	2.44	.103	2.86
4	0.01 *N* HCl + 0.7% NaCl	2.68	.069	4.01
5	0.001 N NaOH	5.13	.144	2.85
6	0.1 *N* acetate buffer	5.44	.061	3.96

[a] *s* depressed by hydration, possibly.

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[16] Svedberg, *Kolloid-Z.* (Erganzungsband) **36,** 63, 64 (1925); Nichols, "Sixth Colloid Symposium," 1928, p. 298.

accounting for the extremely small change from 0.001 *N* HCl solutions to 0.01 N HCl solutions. The apparently greater effect in alkaline solution is in line with the higher asmotic pressure found by Loeb[17] on the alkaline side of the isoelectric point as compared with that on the acid side.

Figure 2 represents the variation of the sedimentation constant with *Ph* for unbuffered solutions compared with the variation in osmotic pressure over the same range found by Loeb.[17] The agreement of maxima and minima is fairly good. On the acid side of the isoelectric point the maximum osmotic pressure occurs at a *Ph* of 3.4. It probably agrees within experimental error with the minimum sedimentation constant which occurs at a *Ph* of 3.0 approximately; the minimum osmotic pressure in the isoelectric region appears to be at a slightly higher *Ph* than the maximum sedimentation constant, which occurs at a *Ph* of 4.65, corresponding closely to Tiselius' value of 4.6 from cataphoresis measurements. The significance of the rapid increase of the sedimentation constant below a Ph of 2 will be explained further on. It should also be noticed that both the s-values and the osmotic pressures experience a greater change on the alkaline side than on the acid side.

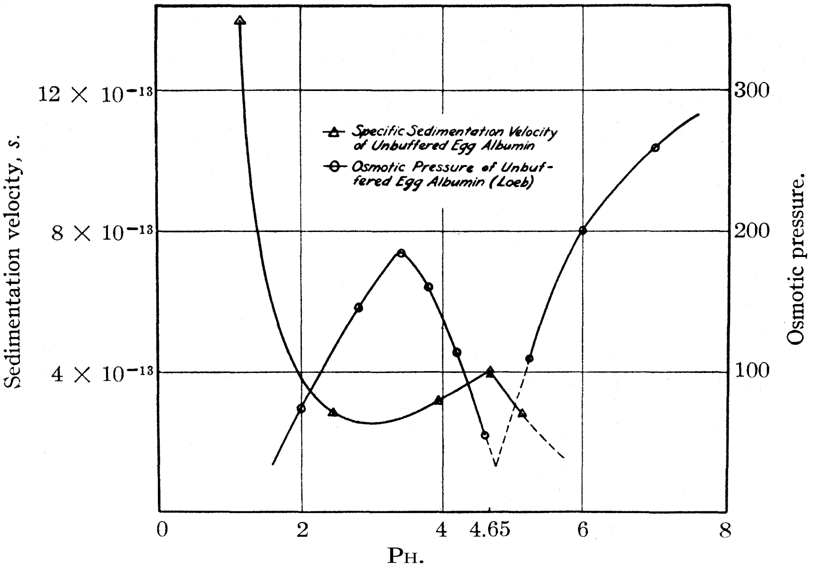

Fig. 2:—Dontian effect on sedimentation velocity of egg albumin.

Figure **3** shows the variation of the sedimentation constant with *Ph* for buffered and unbuffered solutions of egg albumin. The s-value for buffered solutions as drawn appears to be nearly constant over a considerable

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[17] J. Loeb, "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Co., New York, 1st ed., 1922, p. 75, Fig. 18 and p. 118, Fig. 39.

range but may decrease slightly (possibly owing to hydration if this decrease is subsequently verified) on the acid side of the isoelectric point, return to the normal value found for the isoelectric region at a *P_H* of about 2.4 and then join the upward arm of the unbuffered curve at some point; that is, denaturation may be taking place to an increasing extent from a PH of 2.5 down.

Acid-Denaturation.—When the egg albumin is made still more acid, 0.102 N HCl solution, PH 1.16, it is evident (Fig. 3) that a profound change occurs. In a solution of 0.1 N HCl the protein grows more and more viscous on standing and the opalescence increases as well. A 4.0% solution of egg albumin sets in a few hours to a stiff gel. In a 1.0% solution the viscosity at 30° increases from 0.00853 to 0.01057 in eleven hours. The solution centrifuged was considered to have an age of three hours or a viscosity of 0.00908 at 30°.

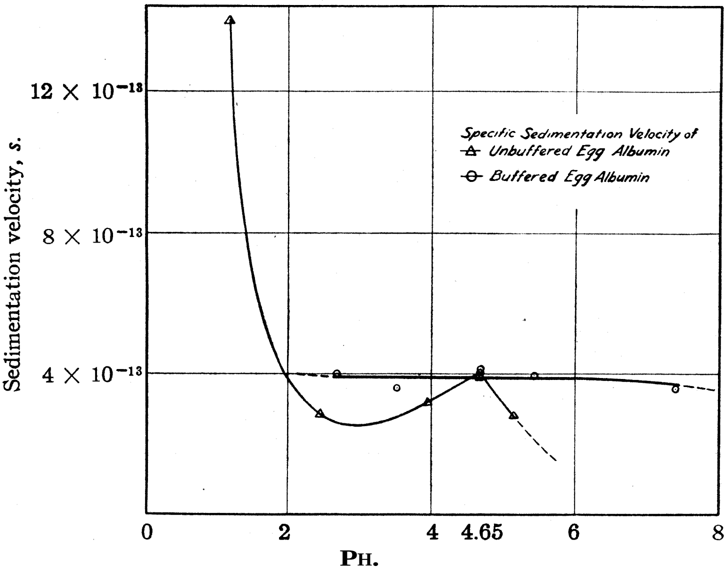
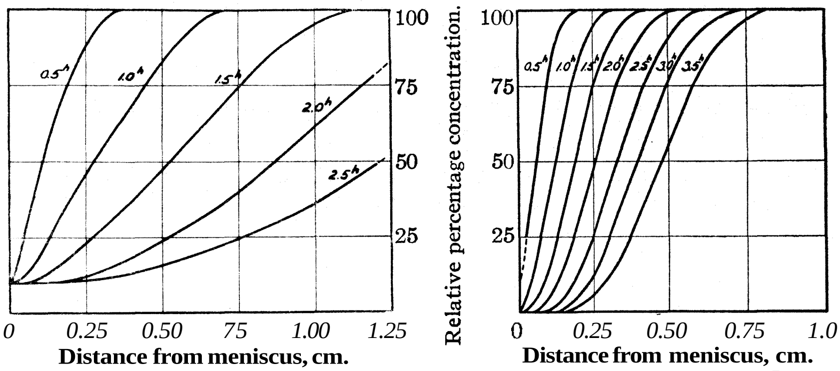


Fig. 3.—Repression of Donnan effect on sedimentation velocity of egg albumin by addition of salts.

The extreme difference in character of the concentration curves for the egg albumin in 0.1 N HCl solution from those obtained for egg albumin in isoelectric buffer is shown in Fig. 4. The time interval between successive curves was half an hour in each case and the experimental conditions were practically the same for the two solutions. There was some increase in light absorption in the highly acid protein and about 10% of uncentrifugible material was present. The rapid sedimentation indicates a rather large increase in size of the effective particle, yielding a rough s-value of 14.0 ×

10^{-13} cm./sec. as compared with the normal value of 4.0×10^{-13} for a molecular weight of **34,500.** The protein has evidently been denatured by the strong acid and has aggregated to gel clumps. Any Donnan effect may be neglected on account of the large excess of hydrochloric acid present. Diffusion should also be small enough to be neglected after incipient gelling has set in because of the increase in size of the effective particle, the increase in the gross and the structural viscosity and the relative inaccuracy of the calculations on a changing system.



1% Egg albumin in $0.1N$ HCl P_H 1.16.

1% Egg albumin in 4.7 P_H acetate buffer.

Fig. 4.—Sedimentation curves of acid-denatured and isoelectric egg albumin.

The distribution curve calculated for the run is given in Fig. 5 for the exposures taken after **60, 90, 120** and **150** minutes of centrifuging. The gradual shift of the points obtained from the successive exposures in the direction of larger radii indicates that the system was changing throughout the whole period. Another possible source of error in the calculation of the distribution curve lies in the assumption of a constant light absorption over the range of sizes of particles present. The distribution curve corresponding to thirty minutes of centrifuging is dotted in to indicate that it is far from correct since the limit of the smaller particles comes at such a small radius. It is probable that diffusion was still playing some part at this stage of the gelling and thus that the system was changing the most rapidly during the first hour. The number of molecules per particle is also plotted to give an idea of the range of "molecules" present in the gel clumps formed of the denatured egg albumin.

Thus we see that egg albumin is moderately stable until fairly high acidities and alkalinities are reached and exhibits a strong Donnan effect in the intermediate acidity and alkalinity range if the ionization of the protein is allowed to exert its maximum effect in unbuffered solutions.

A careful investigation of the behavior of egg albumin in the region of high acidities should throw much light on the acid-denaturation of proteins and on gelling phenomena. Similarly, a study of the conditions at high alkalinities will prove of interest because no information has been gained by osmotic methods in this region on account of the action of strong alkali on the membranes.

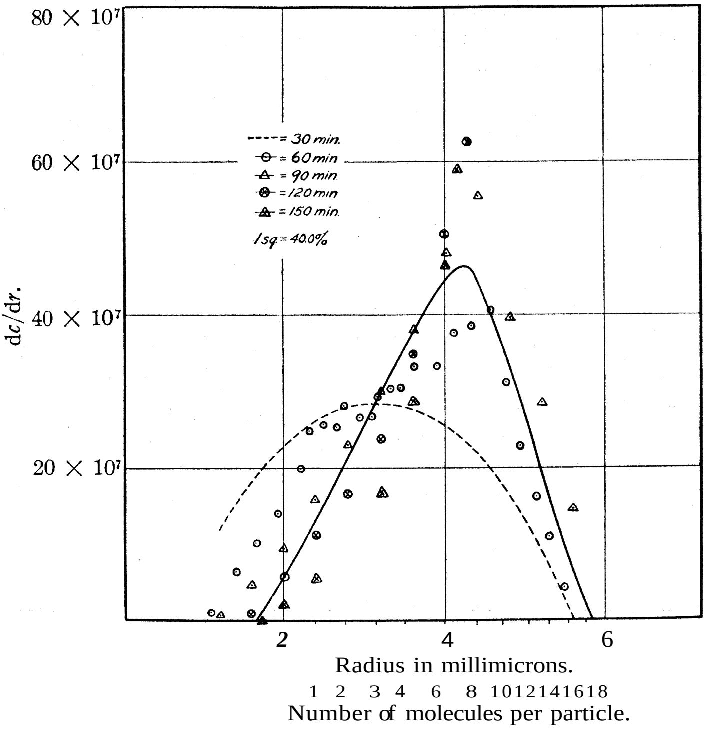


Fig. 5.—Distribution curve for egg albumin in 0.1N HCl

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. Crystallized, electrodialyzed egg albumin has a sedimentation constant of 4.06 X 10^{-13} cm./sec. at 30° but the diffusion constant is abnormal, approximately six-tenths of the required value on the basis of the sedimentation constant and the molecular weight.

2. The molecule is spherical and has a radius of 2.17 mμ; it is practically identical in size and mass with that of Bence-Jones protein, although entirely different in chemical composition.

3. The depression of the sedimentation constant arising from the Donnan effect in unbuffered solutions on either side of the isoelectric point of

egg albumin has been investigated; the maximum depression occurs in the neighborhood of 3.0 **PH.**

4. At a PH of 1.16 in 0.1 *N* hydrochloric acid, egg albumin is completely denatured and gradually forms a gel showing a distribution curve of gel clumps; the mean size corresponds to about seven molecules per particle after three hours.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE PH-STABILITY REGION OF EGG ALBUMIN

BY BERTIL SJÖGREN AND THE SVEDBERG

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An ultracentrifugal study of the molecular weight of egg albumin in electrolyte-free condition near its isoelectric point was carried out by Svedberg and Nichols in 1926.[1] This protein when properly purified was found to be homogeneous with regard to molecular weight. The value arrived at, 34,500 ± 1000, is in good agreement with the result of Sørensen's osmotic measurements, *viz.*, 34,000.[2] In 1927 Nichols made a series of determinations of the molecular weight and the sedimentation constant of egg albumin in the presence of electrolytes within the **PH** region 1.2–7.4.[3] His measurements showed that egg albumin is probably stable from PH 3 to 7. The value of the sedimentation constant arrived at was 4.06 X 10^{-13} at 30°, which corresponds to 3.31 X 10^{-13} at 20°. In acid solution (*P*H 1.16) this protein was found to be completely denatured, gradually forming a gel and showing a distribution curve of gel clumps, the mean size of which corresponded to about seven molecules per particle after three hours.

Since the time when Nichols' determinations were carried out, the ultracentrifugal technique has been further developed and it was, therefore, considered of importance to supplement his measurements by a new and more detailed study of the behavior of egg albumin within a wider PH range.

Preparation of Material and Light Absorption

The egg albumin was prepared according to Sorensen's method[2] with some slight modifications. The material was crystallized three times, the isoelectric state of the crystallizing liquid being checked directly by means of **PH** determinations. The crystals were dissolved in water, dialyzed in the ice box against water and finally electrodialyzed; concentration of stock solution 5.25%. At the time when the determinations were made the material was about three months old.

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[1] T. Svedberg and J. B. Nichols, THIS JOURNAL, 48, 3081 (1926).

[2] S. P. L. Sørensen, *Medd.* Carlsberg Lab., 12,348 (1917).

[3] J. B. Nichols, THIS JOURNAL, 52, 5176 (1930).

Some measurements were also carried out on a similar material which had been kept in the ice box for sixteen months.

The former material did not show any decomposition when submitted to the ultracentrifugal analysis, whereas the latter substance was found to be decomposed to a considerable extent.

The light absorption of solutions of egg albumin at three different hydrogen-ion concentrations was measured by means of the Judd-Lewis spectrophotometer as described in previous communications. The thickness of layer was 2.0 cm. in all measurements and the protein concentration 0.10% at *P*H 2.2 and 5.5 but 0.05% at *P*H 11.2. In Table I the position of the maximum and the minimum of absorption and the values of the extinction coefficients for the maximum and the minimum are recorded. Fig. 1 gives the absorption curves.

TABLE I

LIGHT ABSORPTION OF SOLUTIONS OF EGG ALBUMIN

	M	Solvent	*M*	PH of soln.	Wave length of max. mμ	Wave length of min. mμ	ϵ/c at max.	ϵ/c at min.
HCl	0.007	KCl	0.093	2.2	279	253	8.5	5.0
KH_2PO_4	.095	Na_2HPO_4	.005	6.5	280	255	5.7	2.7
Na_2HPO_4	.026	NaOH	.014	11.2	280	254	10.8	5.6

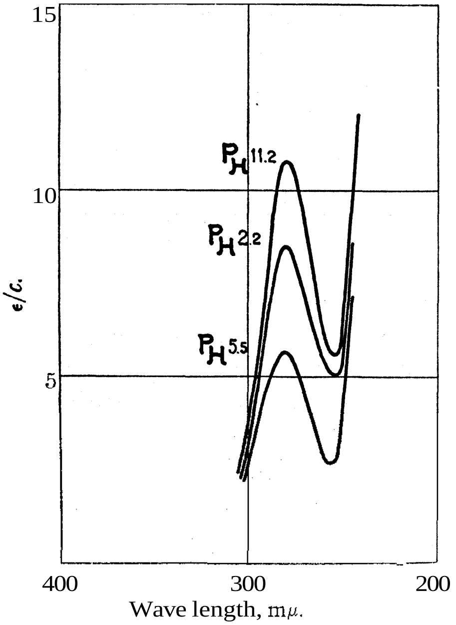

Fig. 1.

As seen from the table the position of the maximum and the minimum does not change with *P*H. The value of the extinction coefficient, however, is much higher in the acid and alkaline solutions than in the solution of *P*H 5.5. The ultracentrifugal analysis described below gives the result that at *P*H values lower than 4 and higher than 9 some of the egg albumin molecules are broken up into a non centrifugible substance. The increase in light absorption is probably due to the presence of this decomposition product.

Determination of the *P*H-Stability Region.—A number of sedimentation velocity runs were made in the oil-turbine ultracentrifuge as described in previous communications. The speed was 40,000–45,000 r. p. m., the temperature in the solution 20–23° and the time of centrifuging three to five hours, The solutions studied were brought to the desired ***PH*** immediately before starting the run. In Table II and Fig. 2 the results are summarized.

TABLE II

EGG ALBUMIN, SEDIMENTATION VELOCITY MEASUREMENTS

	M	Solvent	*M*	*PH* of soln.	Concn of protein. %	$s_{20°}$ X 10^{13} cm./sec.	Non-centrifugible products. %
HCl	0.095	KCl	0.005	1.1	0.25	6.60	55
HCl	.046	KCl	.054	1.4	.20	5.20	35
HCl	.007	KCl	,093	2.15	.20	3.98	10
HAc	,017	NaAc	.003	3.80	.20	3.65	0
HAc	.01	NaAc	.01	4.61	.18	3.43	0
KH_2PO_4	,095	Na_2HPO_4	.005	5.5	.20	3 39	0
KH_2PO_4	.095	Na_2HPO_4	.005	5.5	.45	3.61	0
KH_2PO_4	.095	Na_2HPO_4	.005	5.5	.45	3.53	0
KH_2PO_4	.03	Na_2HPO_4	.03	6.74	.15	3.59	0
KH_2PO_4	.03	Na_2HPO_4	.03	6.74	.15	3.67	0
KH_2PO_4	.005	Na_2HPO_4	.062	7.76	.18	3.37	0
NaOH[a]	.0007	Na_2HPO_4	.03	8.67	.20	3.66	0
NaOH[a]	.001	Na_2HPO_4	.032	9.16	.20	3.77	0
NaOH[a]	.005	Na_2HPO_4	.03	10.28	.12	3.39	20
NaOH[a]	,014	Na_2HPO_4	.026	11.16	.12	3.45	25
NaOH[a]	.017	Na_2HPO_4	.05	11.32	.11	3.31	30
NaOH[a]	.036	Na_2HPO_4	.01	12.46	.07	2.91	40
NaOH[a]	.05			12.63	.05	2.03	50

[a] 1% in NaCl

The sedimentation constant is independent of PH within the range **3** to **11** with a mean value of **3.54** × 10^{-13} at 20°, which is slightly higher **than** the value **3.31** × 10^{-13} calculated from Nichols' determination at 30°. Downward from a ***PH*** of ***4*** and upward from **a** *PH* of 9 the egg albumin

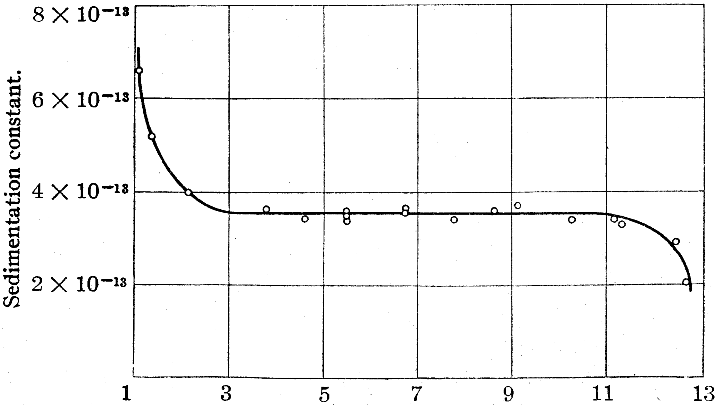

Fig. 2.

molecules begin to dissociate into low-molecular decomposition products. The stability region is, therefore, somewhat smaller than the range within which normal molecules still exist. At high acidities the sedimentation rises rapidly owing to the formation of condensation products as already observed by Nichols. At high alkalinities the sedimentation drops, indicating the breaking up of the protein molecule.

In order to ascertain whether the centrifugible part of the material was homogeneous with regard to molecular weight at the ends of the *P*H-stability range, two sedimentation equilibrium runs were made at *P*H 4.0 and 9.2. In Table III the result is recorded.

TABLE III

EGG ALBUMIN, SEDIMENTATION EQUILIBRIUM MEASUREMENTS

Solvent	*P*H of soln.	Molecular weight
0.016 M in HAc .004 M in NaAc	4.0	33,800, no drift in the values with distance from center of rotation
.032 M in Na_2HPO^4 .001 M in NaOH 1% in NaCl	9.2	34,600, no drift

A sedimentation equilibrium run performed by Nichols at a *P*H of 3.59 gave the value 33,700 for the molecular weight and likewise no drift with distance from center of rotation. It is obvious, therefore, that the centrifugible material is quite homogeneous at the ends of the stability region.

The homogeneity of a sample of egg albumin which had been kept in electrolyte-free solution with toluene as a preservative for sixteen months in the ice box was tested at a *P*H of 5.5 in a sedimentation velocity run and a sedimentation equilibrium run.. The sedimentation constant had increased to about 4×10^{-13} cm./sec. The molecular weight showed strong drift with distance from the center of rotation, the values ranging from 18,100 to 52,000. From these measurements it follows that egg albumin undergoes decomposition and aggregation with time. The same material when new had given a sedimentation constant of 3.4×10^{-13} cm./sec. (O. Lamm).

Discussion of Results

It is of interest to compare the ultracentrifugal behavior of egg albumin with that of Bence-Jones protein using the new value for the sedimentation constant recorded above. As already pointed out by the present authors in a previous communication,[4] egg albumin and Bence-Jones protein are closely related with regard to molecular weight, sedimentation constant s, molar frictional constant f and molecular radius r, the said constants being identical within the limits of experimental error. In Table IV the values of these constants are recorded, the new s-value for egg albumin being used for the calculation; f_s denotes the value of the molar frictional constant to be expected for a spherical molecule of the same density.

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[4] T. Svedberg and B. Sjogrcn, THIS JOURNAL, 51, 3594 (1929).

TABLE IV

MOLECULAR CONSTANTS FOR EGG ALBUMIN AND BENCE-JONES PROTEIN (20°)

Protein	Mol wt.	$s \times 10^{13}$	$f \times 10^{16}$	$f_s \times 10^{-16}$	r, mμ
Egg albumin	**34,500**	**3.54**	**2.47**	**2 47**	**2.17**
Bence-Jones protein	**35,000**	**3 55**	**2.48**	**2 49**	**2.13**

The coincidences borne out by Table IV are even closer than could be expected when taking into account the probable experimental errors of the data. The PH-stability regions of egg albumin and Bence-Jones protein are similar but show some distinct differences. Egg albumin has a somewhat wider stability range than Bence-Jones protein, the stability extending further into the acid as well as into the alkaline regions. The acid decomposition of Bence-Jones protein consists in the splitting-up of some of the molecules into a non-centrifugible substance, leaving some molecules intact, while the decomposition of egg albumin in acid solution is accompanied by the formation of a highly aggregated and rapidly sedimenting substance. In electrochemical respect egg albumin and Bence-Jones protein are quite different, the former having its isoelectric point at PH 4.6 and the latter at 5.2 according to recent determinations by A. Tiselius. The two proteins, although not separable by centrifuging, may easily be separated by means of cataphoresis.

The expenses connected with these experiments have been defrayed by a grant from the foundation "Therese och Johan Anderssons Minne."

Summary

1. The ultracentrifugal methods have been applied to the study of the PH-stability region of egg albumin.

2. In the PH-range 4–9 the protein is stable and homogeneous with regard to molecular weight. The mean value 34,200 is in good agreement with the previous determination by Svedberg and Nichols, *viz.*, 34,500.

3. Below PH 4 and above 9 some of the molecules are split up into a non-centrifugible substance. The sedimentation constant of the centrifugible material is independent of PH within the range 3–11 with a mean value of 3.54×10^{-13} at 20°. The molar frictional constant is 2.47×10^{16} at 20°, which value is identical with the molar frictional constant calculated for a spherical molecule of the same molecular mass and density. The egg albumin molecule, therefore, is spherical and has a radius of 2.17 mμ.

4. At PH values lower than 3, the sedimentation increases, indicating the formation of aggregates of denatured protein; at PH values higher than 9 the sedimentation decreases, indicating the breaking up of the whole material. Both the acid and the alkaline decomposition is accompanied by an increase in the light absorption.

5. A comparison of egg albumin and Bence-Jones protein using the new value of the sedimentation constant for egg albumin shows a still closer

agreement than was formerly found for the molecular constants of these proteins.

UPSALA, SWEDEN

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

THE HYDROGENATION OF ACETOACETIC ESTER AND CERTAIN OF ITS DERIVATIVES OVER NICKEL

BY HOMER ADKINS, RALPH CONNOR AND HOWARD CRAMER

RECEIVED JULY 28, 1930 PUBLISHED DECEMBER 18, 1930

The hydrogenation of acetoacetic ester in the liquid phase with a nickel catalyst has apparently not previously been investigated although Sabatier and Mailhe[1] obtained ethyl butyrate, acetone, isopropyl alcohol, propionic and dehydroacetic acids in a vapor phase reduction over nickel. The methods used in the present investigation were essentially the same as those previously described.[2]

Acetoacetic ester absorbed one mole equivalent of hydrogen when reduced over a nickel catalyst. There were produced small quantities of alcohol and dehydroacetic acid, two parts of ethyl β-hydroxybutyrate and one part of a derivative of this ester, ethyl β-(β'-hydroxybutyryloxy)-butyrate, $CH_3CHOHCH_2CO_2CH(CH_3)CH_2COOC_2H_5$. The ratio of the mono-ester (I) to the di-ester (II) when the reduction was carried out in various solvents is as indicated: no solvent 67% I, 33% II; in ethanol 100% I; in diethyl ether 68% I, 32% II; in methylcyclohexane 68% I, 32% II; in ethyl β-hydroxybutyrate 69% I, 31% II; in *tert.*-butyl alcohol 83% I, 17% 11; in *n*-butanol 66% I and 34% n-butyl β-hydroxybutyrate, b. p. 96–97 (13 mm.). Ethyl a-methylacetoacetate upon reduction gave a mono- and di-ester (ethyl α-methyl-β-(α'-methyl-β'-hydroxybutyryloxy)-butyrate), in the ratio of approximately two parts by weight of the latter to five parts of ethyl α-methyl-β-hydroxybutyrate. However, the dialkyl substituted derivatives of acetoacetic ester, ethyl α,α-dimethylacetoacetate and ethyl a-methyl-a-ethylacetoacetate, gave quantitative reduction to the corresponding α,α-dialkyl-β-hydroxybutyric ester. The formation of the di-esters may be avoided by the use of ethanol, for a quantitative yield of ethyl α-methyl-β-hydroxybutyrate was obtained by reducing ethyl a-methylacetoacetate in that solvent.

The salient facts seem to be: (1) the two beta ketonic esters capable of enolization upon hydrogenation in the absence of a solvent or in the presence of the ethyl-β-hydroxybutyrate or of ether or methylcyclohexane gave large amounts of di-esters along with the simple hydroxy ester.

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[1] Sabatier and Mailhe, Bull. *soc. chim.*, [4] 3,232 (1908).

[2] Adkins and Cramer, THIS JOURNAL, 52,4349 (1930).

(2) The amount of the di-ester was less if tertiary butyl alcohol was used as a solvent and was negligible in the product from the hydrogenations carried on in ethyl or n-butyl alcohols. **(3)** The two keto esters incapable of enolization were hydrogenated quantitatively even without a solvent to the corresponding simple hydroxy esters.

The effect of the alcohols in decreasing the yield of di-ester was not due to the alcoholysis of the di-ester after it was formed, for the alcoholysis of the di-ester was very difficult and did not occur under the conditions in which the alcohols were effective. For example, ethyl β-(β′-hydroxybutyryloxy)-butyrate did not undergo alcoholysis with ethanol upon being heated for three hours at 150° in the reduction apparatus. Only 40% of it was converted to ethyl β-hydroxybutyrate after six and one-half hours at 190°. The resistance of this ester to alcoholysis is further shown by the fact that there was no alcoholysis of the di-ester after it had been refluxed with an ethanol solution of sodium ethoxide for two and one-half hours.

The effectiveness of the alcohols in inhibiting the formation of the di-ester is understandable upon the hypothesis of Arndt and Nachtwey[3] with regard to the formation of dehydroacetic acid from acetoacetic ester. They suggested that two reactions are involved. The first of these was supposed to be reversible since removal of ethyl alcohol permitted the formation **of** dehydroacetic acid, while the second was supposed to be an irreversible reaction, since boiling alcohol did not convert dehydroacetic acid into acetoacetic ester. (It will be shown later that the latter is also a reversible reaction.) These authors suggest that the mechanism of the formation of dehydroacetic acid may be as shown in Reactions I and II

$$CH_3C(O)CH_2COOEt + HOC(CH_3){=}CHCOOEt \rightleftharpoons CH_3C(O)CH_2C(O)OC(CH_3){=}CHCOOEt + EtOH \quad (I)$$

$$CH_3C(O)CH_2C(O)OC(CH_3){=}CHCOOEt \longrightarrow CH_3C(O)\underline{CHC(O)OC(CH_3){=}CHC}{=}O + EtOH \quad (II)$$

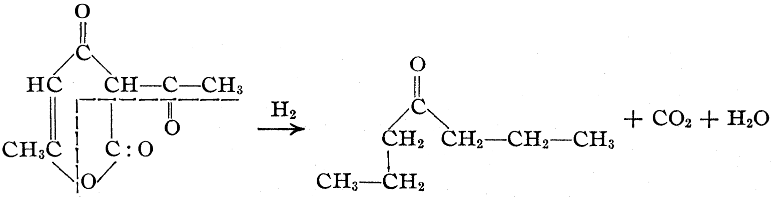
The formation of ethyl β-(β′-hydroxybutyryloxy)-butyrate in the reduction of acetoacetic ester substantiates the mechanism postulated by Arndt and Nachtwey, since it is the reduction product of the intermediate indicated in the formation of dehydroacetic acid from acetoacetic ester. The presence of ethanol would shift the first reaction to the right and thus greatly decrease the amount of $CH_3C(O)CH_2C(O)OC(CH_3){=}CH\text{-}COOEt$ and consequently of the di-ester formed from it by hydrogenation. n-Butanol would behave similarly since there is little difference among the primary alcohols in the concentration at equilibrium in similar reactions such *as* ester and acetal formation. Tertiary butyl alcohol would be expected to be much less effective in shifting the equilibrium toward the left since it is so little active in ester and acetal formation.

[3] **Arndt and** Nachtwey, ***Ber.,*** 57B, 1489 **(1924).**

The rate of reduction of acetoacetic ester in methylcyclohexane or ether was three times as great as in the absence of a solvent; in fact pure acetoacetic ester reduced much more slowly at 150° than it did in the presence of these solvents at 125°. The rate of reduction of an alcoholic solution of the ester was intermediate between that of the pure ester and that in a methylclohexane solution.

The formation of 1 or 2% of dehydroacetic acid in the reduction of acetoacetic ester and the possible relationship of the di-ester obtained to an intermediate in the formation of dehydroacetic acid led to an investigation of the hydrogenation of the latter compound. Dehydroacetic acid was not readily reduced, as from two to five applications of catalyst were necessary in each run before the maximum absorption of hydrogen was obtained. The temperature of reduction was 185–190° and the pressures were from 108 to 325 atmospheres, the reduction going approximately four times as rapidly at the highest as at the lowest pressure.[4] At pressures of about 130 atmospheres three moles of hydrogen per mole of dehydroacetic acid were absorbed, but at a pressure of about 325 atmospheres, five moles of hydrogen were taken up. Methylcyclohexane was used as a solvent for the reduction. It was found that when ethanol was used as a solvent, no reduction occurred, but heating with or without nickel at 190° for two hours gave 70% conversion of dehydroacetic acid to ethyl acetoacetate, the remainder of the acid being recovered unchanged.

The chief product obtained in the hydrogenation of dehydroacetic acid was heptanone-4, the yield being 40 to 45% under the optimum conditions. The formation of this ketone must involve the removal of oxygen and decarboxylation as well as hydrogenation, e. g.



The water formed in the removal of the oxygen would hydrolyze dehydroacetic acid[6] and the products under reducing conditions would presumably give acetone, acetic acid and isopropyl and ethyl alcohols. These alcohols would in turn bring about the formation of acetoacetic ester through the alcoholysis of dehydroacetic acid. These compounds except acetic acid were all found among the reduction products of dehydroacetic acid.

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[4] Adkins, Cramer and Connor, unpublished work

[5] Collie, J. Chem. *Soc.*, **59**, 179 (1891).

It is noteworthy that in the hydrogenation of dehydroacetic acid in methylcyclohexane and in the attempted hydrogenation in ethanol, there were formed compounds (acetone, heptanone-4 and acetoacetic ester) which are readily hydrogenated under the conditions of temperature and pressure at which they were formed. This is not due to the action of dehydroacetic acid, for acetoacetic ester in a mixture of it with dehydroacetic acid was readily hydrogenated but the acetoacetic ester produced by the dehydrogenation of the dehydroacetic acid was not reduced. This was indicated by the hydrogen absorption and by the evidence for acetoacetic ester in the reaction product.

Experimental Part

A summary of typical results obtained in the reduction of acetoacetic ester and some of its derivatives is given below. There is given in

TABLE I

REDUCTION OF VARIOUS DERIVATIVES OF ACETOACETIC ESTER

No.	Compound	Moles	Moles H_2	Catalyst G.	Catalyst No. (portions)
1	Acetoacetic ester	0.39	0.39	2	1RAC
2	Acetoacetic ester	.39	.40	2	1RAC
3	Acetoacetic ester	39	.43	2	1RAC
4	a-Methylacetoacetic ester	.35	.37	2	4RAC
5	a-Methylacetoacetic ester	1.04	1.06	4	5RAC
6	a-Methyl-a-ethylacetoacetic ester	0.28	0.32	2	3KF
7	α,α-Dimethylacetoacetic ester	.62	.64	3	4KF
8	Dehydroacetic acid	.30	. .	20	1RAC (5)
9	Dehydroacetic acid	3.0	.90	11	1RAC (3)
10	Dehydroacetic acid	.30	1.48	11	5RAC (3)
11	Dehydroacetic acid	.12	0	None or 3g1RAC	
12	Dehydroacetic acid	.21	1.0	4	5RAC

No.	Ml.	Solvent	Temp., °C.	Press., Atm.	Time, Hours	Yield, %
1		None	125	94±11	4.5	B67 mono-ester B33 di-ester
2	50	EtOH	125	89±15	2.5	B100 mono-ester
3	50	C_7H_{14}	125	103±14	1.5	B68 mono-ester B32 di-ester
4	50	EtOH	150	110±7	0.75	A85, B100 mono-ester
5		None	175	160±24	9	A52, B70 mono-ester A19, B26 di-ester
6		None	175	150±10	3	B100 mono-ester
7		None	185	150±10	2	B100 mono-ester
8	100	C_7H_{14}	185	132±16	21	See exptl. part
9	100	C_7H_{14}	185	174±18'	10.5	See exptl. part
10	100	C_7H_{14}	185-190	332±41	8.5	See exptl. part
11	50	EtOH	190	165	2	C70 acetoacetic acid C30 dehydroacetic acid
12	0.42 moles of acetoacetic ester		190	132±28	3	See exptl. part

order, the name and amount in moles of the compound reduced, the moles of hydrogen absorbed, the weight and number of the catalyst according to our records, the volume and name of solvent when one was used, the temperature, pressure and time for reduction after reaching the designated temperature, the name and yield of product(s). The yields marked "A" are those actually obtained while in those marked "B" allowance is made for the mechanical losses in handling the materials during reduction and filtration, and in "C" for mechanical losses and for the amount of the starting material recovered unchanged.

The product from 50 g. of acetoacetic ester after separation of the nickel catalyst in a typical experiment weighed 45 g. It gave no coloration with a ferric chloride solution and upon fractionation through a 20-cm. Widmer column gave two main fractions: 28 g. 77–79" (15 mm.) and 13 g. 154–156° (15 mm.). The remainder (4 g.) distilled below, between and above these fractions. The part distilling below the two main fractions was identified as ethanol through the formation of its 3,5-dinitrobenzoate. The part distilling above the two main fractions contained dehydroacetic acid, m. p. 110°. The fraction boiling at 77–79° (15 mm.) was ethyl β-hydroxyethylbutyrate. The fraction boiling at 154–156° (15 mm.) was identified as ethyl β-(β′-hydroxybutyryloxy)-butyrate on the basis of the following experimental findings. Upon saponification ethanol, identified as the 3,5-dinitrobenzoate, was formed. The acid so produced was a white rancid-smelling solid melting at 72° and boiling at 184° (740 mm.). It rapidly reduced cold alkaline permanganate solution, showed a neutral equivalent of 87, and gave a dibromide melting at 85–86.5°. Crotonic acid melts at 72°, has a neutral equivalent of 86 and its dibromide melts at 87°. The ester showed a saponification number of 109.5 and 110.3, d_{25}^{25} 1.0678, n_{D}^{25} 1.4360, and a molecular refraction of 53.36 ($\mathrm{MR'_D}$). The calculated saponification number for the di-ester is 109 and the $\mathrm{MR'_D}$ 53.39.

Anal. Calcd. for $C_{10}H_{18}O_5$: C, 55.05; H, 8.25. Found: C, 54.97; 54.70; H, 8.30, 8.33.

The ester showed no alcoholysis when 15 g. was boiled for two and one-half hours in 50 ml. of ethanol containing 6.8 g. of sodium ethoxide, nor when it was heated with ethanol alone for three hours at 150° under a pressure of 130 atmospheres of hydrogen. However, 40% of it was converted to ethyl β-hydroxybutyrate in six hours at 190°. Butyl β-hydroxybutyrate was identified on the basis of the facts that it showed a saponification value of 157 and 160 (theoretical 160) and gave n-butanol, identified as the dinitrobenzoate, upon saponification.

The fractionation of the products from the reduction of ethyl a-methylacetoacetate showed 1.4% ethanol, 70.5% ethyl α-methyl-β-hydroxybutyrate, b. p. 85–87° (22 mm.), 26% ethyl α-methyl-β-(α′-methyl-β′-hydroxybutyryloxy)-butyrate, b. p. 155–158° (17 mm.), and 1.4% residue. The ethyl α-methyl-β-(α′-methyl-β′-hydroxybutyryloxy)-butyrate was characterized by a saponification number of 124.4 and 124.1 (calcd. 123), d_{25}^{25} 1.0332, n_{D}^{25} 1.4393, $\mathrm{MR'_D}$ 62.65 (calcd. 62.59).

Anal. Calcd. for $C_{12}H_{22}O_5$: C, 58.53; H, 8.94. Found: C, 58.29, 58.49; H, 8.94, 8.81. The acid corresponding to this ester has been prepared previously.[6]

Dehydroacetic Acid.—In the runs made at 130 atmospheres three main fractions, besides the solvent, were obtained upon distilling the reduction product of dehydroacetic acid. The first of these comprised 23% of the recovered material and contained ethyl

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[6] Wislicenus, *Ber.*, 8, 1036 (1875); Rohrbeck, Ann., 188,229 (1877); *cf.* Skau and Saxton, THIS JOURNAL, 52, 335 (1930).

alcohol, acetone and water. The second was heptanone-4, b. p. 144–146° (735 mm.), and comprised 17.3% of the material recovered, while the third fraction was acetoacetic ester, b. p. 178" (735 mm.), and amounted to 29.8%. When the latter fraction was collected over a four degree range, 174–178° (735 mm.), enough butyric acid was present after hydrolysis to obtain as derivatiyes, the anilide and the *p*-bromo-anilide. The 30% of the material not included here represents the transition material between fractions, and about 7.6% of unreduced material.

The fractionation of the products from the hydrogenation of dehydroacetic acid at 325 atmospheres gave amounts of compound boiling below 140° similar to those obtained in the hydrogenation at lower pressures but there was approximately two and one-half times as much heptanone-4 as under those conditions. There was less than half as much material boiling above the range of heptanone-4 with no evidence of the presence of acetoacetic ester. Unquestionably ethyl β-hydroxybutyrate and probably ethyl β-(β′-hydroxybutyryloxy)-butyrate were present in the high fractions but the total amount (3 g.) was too small and impure to obtain crystalline derivatives.

The presence of ethanol and of acetone among the reduction products of dehydroacetic acid was demonstrated through the formation of the 3,5-dinitrobenzoate of the former and the dibenzal derivative of the latter. Heptanone-4 was characterized by its boiling point 145–146° and the melting point of its semicarbazone (133–134") and the melting point (133–134°) of a mixture of this semicarbazone with some known semicarbazone of this ketone. It was further characterized by reduction over nickel at 175° and 160 atmospheres to heptanol-4, b. p. 152–154 (740 mm.), which gave a 3.5-dinitrobenzoate melting at 64° and an a-naphthylurethan melting at 79–80".

Anal. Calcd. for $C_{18}H_{32}NO_2$: C, 75.52; H, 8.39. Found: C, 75.68, 75.58; H, 8.34, 8.25.

The fraction, b. p. 170–174° (740 mm.), was characterized as acetoacetic ester by its boiling range and its coloration with ferric chloride solution, by the formation of acetone and ethanol through alkaline hydrolysis. The fraction gave a vigorous reaction with phenylhydrazine but the reaction product was an oil which could not be purified.

Dehydroacetic acid was prepared as by Arndt and Nachtwey.[7] Three hundred grams of acetoacetic ester in a 500-ml, flask was heated so that the vapors reaching the top of a 60-cm. Vigreux column had a temperature of 78–85". After 40 g. of ethanol had distilled, 34.4 g. of dehydroacetic acid separated out on cooling the contents of the reaction flask. Fifteen grams of ethanol was then distilled out and 29.5 g. of dehydroacetic acid obtained; further heating gave successively 8.3 g. of ethanol, 14.5 g. of the acid and 10 g. of ethanol and 17.5 g. of the acid. The total yield from 300 g. of the ester was 96 g. or 50% of the theoretical yield. Much lower yields were obtained when attempts were made to distil out all the ethanol without the removal of the dehydroacetic acid from time to time as indicated. The product had a melting point of 98–103°, and 109–110" after recrystallization from ethanol and water. The product used for reduction was not so purified.

Summary

Ethyl acetoacetate readily took up one molecular equivalent of hydrogen over a nickel catalyst at temperatures from 100 to 150°. If the hydrogenation was carried out in an ethanol solution, ethyl β-hydroxybutyrate was formed practically quantitatively. In the absence of a solvent or in ether or methylcyclohexane, there was formed along with two parts of ethyl β-hydroxybutyrate, one part of a derivative of it,

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[7] Arndt and Nachtwey, Ber., 57B, 1487 (1924).

ethyl β-(β'-hydroxybutyryloxy)-butyrate. This ester despite the fact that it is the ester of a secondary alcohol did not undergo alcoholysis at the temperature used for the reduction of acetoacetic ester or in a boiling alcoholic solution of sodium ethoxide. It did undergo alcoholysis at 190° in the presence of a nickel catalyst. This complex ester appears to be formed through the reduction of two molecules of acetoacetic ester with the elimination of one molecule of ethanol. This condensation product was postulated by Arndt and Nachtwey as an intermediate in the formation of dehydroacetic acid from acetoacetic acid, so that the results here reported support their hypothesis. The methyl derivative of acetoacetic ester on reduction behaved similarly to the unsubstituted ester. The α,α-dimethyl and the a-methyl-a-ethylacetoacetic ester reduced smoothly to the corresponding simple hydroxy ester either with or without a solvent since there is no possibility of the formation of a complex ester analogous to that formed from the 8-ketonic esters capable of enolization.

Dehydroacetic acid appears to give heptanone-4 as the chief product in hydrogenation over nickel. The use of hydrogen pressure in excess of 300 atmospheres appears not only very greatly to accelerate the rate of hydrogenation but to favor the formation of heptanone-4 with a decrease in the products formed through the hydrolysis and alcoholysis of the dehydroacetic acid. Dehydroacetic acid has been found to undergo a smooth alcoholysis to acetoacetic ester at 190°.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

THE STRUCTURE OF PARA-DIMETHYLAMINOBENZOIN[1]

BY SANFORD S. JENKINS[2] WITH LUCIUS A. BIGELOW AND JOHANNES S. BUCK

RECEIVED JULY 30, 1930 PUBLISHED DECEMBER 18, 1930

In the preceding paper, dealing with the reduction of *p*-dimethylaminobenzil,[3] it was found that the corresponding benzoin, on treatment with tin and hydrochloric acid in alcohol solution, yielded two isomeric desoxy derivatives, designated as *a*- and β-forms, the structures of which were established. This fact made it seem possible that the benzoin itself might be a mixture of *a*- and @-modifications, which, at least theoretically, would be expected to exist.

Accordingly, efforts were made to separate the apparently pure benzoin (m. p. 163–164°) into isomeric components by ordinary methods. For

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[1] This paper is in part constructed from portions of a thesis presented by Sanford S. Jenkins in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences, Duke University.

[2] Angier B. Duke Memorial Fellow, **1929–1930.**

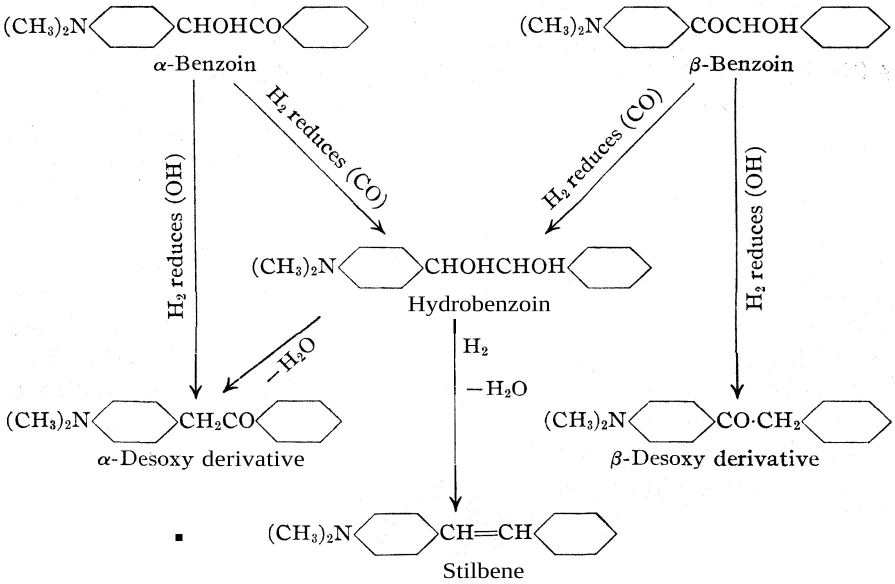
[3] Jenkins, Buck and Bigelow, THIS JOURNAL, **52,4495 (1930).**

instance, the material was repeatedly fractionally crystallized, both from glacial acetic acid and from alcohol, but, while the melting points of the different fractions varied slightly, when samples of these were mixed with the pure substance, there was no depression. Also, pure *p*-dimethylaminobenzil was reduced catalytically to the benzoin in the Adams apparatus, employing different solvents, in the hope of obtaining isomers, but in every case mixed melting points of the products with an authentic sample of the benzoin showed no depression.

H. Staudinger,[4] who first prepared *p*-dimethylaminobenzoin by condensing *p*-dimethylaminobenzaldehyde with benzaldehyde in the presence of potassium cyanide, states unequivocally that the product (m. p. 163–164°) can be but a single substance having the constitution expressed by the formula *p*-$(CH_3)_2NC_6H_4CHOHCOC_6H_5$, which we designate as the a-form. Certain experimental data, which form the basis for considerable speculation, are advanced in support of this assertion.

In spite of the fact that the present writers were not able to separate the benzoin into a- and β-components, they were led to doubt the validity of the conclusion reached by the earlier investigator on the basis of the following considerations.

As shown in the preceding paper, already cited, the reduction of the benzoin with tin and hydrochloric acid yields both the a- and β-desoxy derivatives, but the dehydration of the hydrobenzoin with a mixture



THE POSSIBLE REDUCTION PRODUCTS OF α- AND β-*p*-DIMETHYLAMINOBENZOIN

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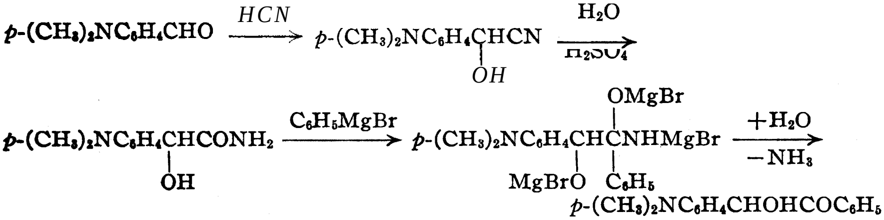
[4] Staudinger, *Ber*, 46, 3530, 3535 (1913).

of acetic and hydrochloric acids gives only the a-isomer. Furthermore, the action of tin and hydrochloric acid on the hydrobenzoin produces only the corresponding stilbene. From this it follows, upon theoretical considerations, that the a-form of the benzoin cannot, upon reduction, yield both desoxy compounds, whereas the β-modification, or a mixture of the two, can do so. The reasons for these statements may be made clear by reference to the diagram.

Thus, it did not seem possible that "ordinary" *p*-dimethylaminobenzoin, prepared according to Staudinger, which does yield two desoxy compounds upon reduction, could consist solely of the a-modification.

The writers, therefore, decided to attempt the synthesis of the a- and β-benzoins, by means of such methods as would establish definitely the structures of these substances. Accordingly, *p*-dimethylaminobenzaldehyde was treated with anhydrous hydrocyanic acid, and the resulting cyanohydrin hydrolyzed to form *p*-dimethylaminomandelamide, as described by Sachs.[5] The procedure was considerably modified, however, and is given in detail further on. The amide was then condensed with phenylmagnesium bromide according to the general method of McKenzie and Wren,[6] with the formation of the desired a-p-dimethylaminobenzoin of undoubted structure. The reactions may be expressed as follows:



$$p\text{-}(CH_3)_2NC_6H_4CHO \xrightarrow{HCN} p\text{-}(CH_3)_2NC_6H_4\underset{\underset{OH}{|}}{C}HCN \xrightarrow[H_2SO_4]{H_2O}$$

$$p\text{-}(CH_3)_2NC_6H_4\underset{\underset{OH}{|}}{C}HCONH_2 \xrightarrow{C_6H_5MgBr} p\text{-}(CH_3)_2NC_6H_4\underset{\underset{MgBrO}{|}}{C}H\overset{\overset{OMgBr}{|}}{\underset{\underset{C_6H_5}{|}}{C}}NHMgBr \xrightarrow[-NH_3]{+H_2O}$$

$$p\text{-}(CH_3)_2NC_6H_4CHOHCOC_6H_5$$

a-p-Dimethylaminobenzoin

The product, after crystallization from alcohol, melted at 159–160° (corr.). It gave on analysis the correct values for carbon, hydrogen and nitrogen and it had the molecular weight indicated by the formula. Upon oxidation with Fehling's solution, it formed the known benzil, and, when reduced with tin and hydrochloric acid in alcohol solution, it yielded only the a-desoxy derivative, not a trace of the β-isomer being formed. This was to be expected from the theoretical considerations already outlined.

When the new benzoin was mixed with the corresponding substance, prepared according to Staudinger, the melting point was depressed 15–18°, indicating clearly that the two compounds are different. These facts appear to prove with certainty that *p*-dimethylaminobenzoin prepared by the potassium cyanide condensation method is not the α-isomer.

It remained to be ascertained, however, whether the so-called "ordi-

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[5] Sachs and Lewin, *Ber.*. 35,3571 (1902).

[6] McKenzie and Wren, J. *Chem. Soc.*, 93,311 (1908).

nary" benzoin was the pure β-isomer, or a mixture of the two forms which was uncommonly difficult to separate. Either possibility accorded with the known facts at this time. Having had success with the method outlined above in the synthesis of the a-derivative, the writers decided to prepare the @-benzoin by an analogous procedure. Mandelamide was therefore synthesized, as described by McKenzie and Wren, in their paper already cited, and condensed with p-dimethylaminophenylmagnesium bromide. The Grignard reagent was prepared by refluxing *p*-bromodimethylaniline with magnesium, activated with a little ethyl bromide. The reaction was sluggish, however, and the yield not very favorable. The condensation took place in a manner similar to that already illustrated, and must lead to the β-benzoin.

The product, after crystallization from alcohol, melted at 163–164°. It also gave, on analysis, the correct values for carbon, hydrogen and nitrogen. On oxidation, it formed the benzil, and on reduction with tin and hydrochloric acid in alcohol solution it yielded both the α- and @-desoxy derivatives. When it was mixed with the a-benzoin, the melting point was sharply depressed, but when the corresponding substance, prepared according to Staudinger, was added, no change in the melting point was observed.

It therefore seems certain that p-dimethylaminobenzoin prepared by the potassium cyanide condensation method is a single substance, consisting of the β- and not the a-isomer, and having the structure *p*-$(CH_3)_2NC_6H_4COCHOHC_6H_5$.

It appears to the writers that the only conclusion which it is possible to draw from the facts here reported is that in this instance the assertion of the earlier investigator cannot be sustained.

Experimental

_p_-Dimethylaminobenzaldehyde Cyanohydrin.—The method finally adopted for the preparation of this substance was a modification of that described by Sachs and already cited. It was not found possible, however, to obtain results, using liquid hydrogen cyanide synthesized according to Wade and Panting' until it was noticed that a trace of calcium chloride, which was carried into the apparatus by chance, catalyzed the reaction. This fact, together with the observations that hydrocyanic acid of German manufacture containing calcium chloride as a drying reagent, produced results, while purified calcium chloride did not, made it evident that the actual catalyst was calcium oxide, contained in the commercial chloride. In the presence of a trace of the oxide. the reaction took place without the slightest difficulty. The detailed procedure consisted in placing 10 g. of p-dimethylaminobenzaldehyde and about 0.2 g. of calcium oxide in a thick-walled bottle of 400-cc. capacity, cooled in a freezing mixture. Ten cc. of anhydrous hydrogen cyanide was then distilled into the bottle, which was tightly corked and heated to 40–45° in a water-bath until the reaction mixture had solidified, requiring about thirty-five minutes. The excess hydrogen cyanide was removed by

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[7] Wade and Panting, J. *Chem. Soc.*, 73,256 (1898).

suction and the solid residue dissolved in 50 cc. of warm chloroform. Finally, ligroin (b. p. 60–70") was added until precipitation appeared to be complete. The white solid cyanohydrin was filtered off and dried. It weighed 7 g., which is 59% of the theoretical, melted at 110–113° and was sufficiently pure for use in the subsequent work.

p-**Dimethylaminomandelamide.**—This compound was also prepared by Sachs, but the details given are rather meager. The writers proceeded as follows. Four grams of the cyanohydrin was dissolved in approximately 10 cc. of sulfuric acid (sp. gr. 1.84) and the mixture allowed to stand for about fifteen minutes. After this it was poured slowly, with constant shaking, into a slush of ice and water. Then the solution was carefully neutralized with ammonia (sp. gr. 0.90). During these operations care was taken that the temperature at no time rose above 15". Just before the neutral point was reached a brown amorphous precipitate was formed, which was filtered off and discarded. The resulting neutral mixture was allowed to stand in the ice box overnight, when the amide crystallized out A further quantity was obtained on evaporating the mother liquor. The product weighed 2 g. (45% of the theoretical), and after two crystallizations from water melted at 184–186° (uncorr.). The yields obtained in different runs varied considerably.

α-*p*-**Dimethylaminobenzoin.**—A mixture of 30 g. of bromobenzene, 5.5 g. of magnesium turnings and 50 cc. of anhydrous ether was refluxed until most of the metal had dissolved. Then 2.5 g. of finely powdered *p*-dimethylaminomandelamide was added, in small portions, over a period of fifteen minutes. After each addition of the amide, a vigorous reaction occurred, which was allowed to subside before the next portion was added. After heating on the water-bath for twelve hours the solution was poured into 200 g. of crushed ice containing 30 g. of concd. sulfuric acid. The ether was removed, and the aqueous layer extracted with two 100-cc. portions of ether. The extracts were discarded. The acid solution was then neutralized with ammonia and the yellow precipitate which formed was separated, dissolved in 50 cc. of alcohol and filtered hot. On cooling, a mass of yellow needles separated which weighed 1.5 g. (45%) and melted at 152–153°. After three recrystallizations from alcohol, the product melted at 159–160" (corr.). When this was mixed with a sample of the benzoin prepared according to Staudinger, the melting point was depressed 12–18".

Anal. Calcd. for $C_{16}H_{17}NO_2$: C, 75.29; H, 6.67; N, 5.49; mol. wt. 255. Found: C, 75.19; H, 7.02; N (Kjeldahl), 5.58, 5.29; mol. wt. (in benzene), 258.

Oxidation of α-*p*-**Dimethylaminobenzoin.**—About 0.10 g. of the benzoin dissolved in 10 cc. of alcohol was heated on the water-bath with concentrated Fehling's solution for one hour, after which the cuprous oxide was filtered off and the mixture diluted with 50 cc. of water. On standing a yellow crystalline precipitate formed, which was removed by filtration and recrystallized from 60% alcohol. The product melted at 115–116° and a mixed melting point taken with known *p*-dimethylaminobenzil showed no depression.

Reduction of α-*p*-**Dimethylaminobenzoin.**—The reduction was carried out by treating 1.0 g. of the benzoin with 1.0 g. of mossy tin, 5 cc. of hydrochloric acid (sp. gr. 1.19), 0.10 g. of copper sulfate pentahydrate and 20 cc. of alcohol. The solution was refluxed for five hours, filtered hot and diluted with 30 cc. of water. After standing overnight, no precipitate whatever had formed, indicating the absence of the β-desoxy derivative, which is relatively insoluble in dilute acid mixtures. The solution was then made alkaline with ammonia and filtered, after which the yellow precipitate was extracted with 100 cc. of boiling alcohol. The extract was evaporated to a volume of about 25 cc. and allowed to stand.

The product which separated consisted of long white prisms which weighed 0.70 g. (74%) and melted at 127–128°. When it was mixed with known α-*p*-dimethylaminodesoxybenzoin, no depression in the melting point was observed.

An exactly parallel reduction of p-dimethylaminobenzoin prepared according to Staudinger, yielded 0.30 g. of the a-desoxy compound and 0.47 g. of the β-desoxy derivative. In this case the total yield was 0.77 g., which is 82% of the theoretical quantity.

β-*p*-Dimethylaminobenzoin.—A mixture of 30 g. of p-bromodimethylaniline, 3.1 g. of magnesium turnings and 75 cc. of absolute ether was refluxed for forty-eight hours. To start the reaction, about 12 drops of ethyl bromide was added in two portions. After the heating, 1.5 g. of finely powdered mandelamide, prepared according to McKenzie and Wren,[8] was added in small portions, over a period of ten minutes. A vigorous reaction ensued after each addition. The solution was then refluxed for fifteen hours more. and poured into 200 g. of crushed ice which contained 20 g. of sulfuric acid (sp. gr. 1.84). The clear yellow aqueous layer was extracted six times with 50-cc. portions of ether and, in this case, the aqueous layer was discarded. The ether was removed by distillation and the solid residue, after one crystallization from a small amount of alcohol, weighed 0.7 g. (25%) and melted at 159–161°. After two further recrystallizations from alcohol the product formed stout yellow needles melting at 161–162° (corr.). When a sample of this was mixed with the benzoin prepared according to Staudinger, the melting point was not depressed.

Anal. Calcd. for $C_{16}H_{17}NO_2$: C, 75.29; H, 6.67; N, 5.49. Found: C, 75.43; H, 7.04; N (Kjeldahl), 5.28, 5.39.

Oxidation of **β-*p*-Dimethylaminobenzoin.**—The reaction was performed by heating 0.12 g. of the benzoin, dissolved in 15 cc. of alcohol, with Fehling's solution. The mixture was heated on the water-bath for three-fourths of an hour and the reagent added in small portions until no further action occurred. The cuprous oxide was filtered off, the solution diluted with 50 cc. of water and the precipitate which formed on standing filtered and recrystallized from 15 cc. of 60% alcohol. The product formed yellow prisms melting at 116–117°, and weighing 0.072 g., which is 60% of the theoretical. When it was mixed with a sample of known *p*-dimethylaminobenzil, the melting point was not depressed.

Reduction of **β-*p*-Dimethylaminobenzoin.**—The reduction was carried out in a manner similar to that described for the case of the a-isomer. After the reaction was complete, the mixture was allowed to stand in the cold and the β-desoxy derivative separated. It weighed 0.20 g. and on crystallization from alcohol formed plates melting at 163–164°. The mother liquors from the reduction mixture were worked up as already described, and yielded 0.50 g. of the a-desoxybenzoin. After this had been purified in the usual way, it melted at 127–128°. The combined yields of the α- and p-isomers amounted to 0.70 g., which is 74% of the theoretical amount. When samples of these were mixed with known α- and β-*p*-dimethylaminodesoxybenzoin, respectively, the melting points were not depressed.

Reduction of ***p*-Dimethylaminohydrobenzoin.**—In order to show that no p-desoxybenzoin results from the reduction of the hydro derivative even with tin and hydrochloric acid in alcohol solution, the following experiment was carried out: 2.55 g. of "ordinary" p-dimethylaminobenzoin was dissolved in 50 cc. of absolute alcohol and reduced to the hydro compound in the Adams apparatus, in the presence of 0.1 g. of platinum oxide. The method is essentially identical with those described in the preceding paper, already cited. The catalyst was filtered off, and, without isolating the product, 3 g. of tin, 10 cc. of hydrochloric acid (sp. gr. 1.19) and a crystal of copper sulfate pentahydrate were added to the solution, which was refluxed for six hours. The unchanged tin was filtered off, and 90 cc. of water added. On standing, no precipitate appeared, so the mixture was neutralized with sodium carbonate, and the resulting product filtered, washed and extracted with alcohol. On cooling, the extract deposited colorless scales weighing 1.9 g. and melting at 147–148". When these were mixed with known *p*-dimethylamino-

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[8] McKenzie and Wren, J. *Chem. Soc.*, 93,311 (1908).

stilbene, the melting point was not depressed, thus determining the identity of the product. The yield was 85%.

Summary

1. α- and β-*p*-Dimethylaminobenzoin have been synthesized by the Grignard method, leaving no reasonable doubt as to their structures.

2. The reduction products of these isomers have been studied and correlated with the corresponding substances produced by reducing p-dimethylaminobenzoin as prepared by condensing the corresponding aldehydes in the presence of potassium cyanide.

3. *p*-Dimethylaminobenzoin, as prepared by the condensation method, is shown to be the 8-isomer, and not the a-derivative, as was hitherto supposed. It has the structure *p*-$(CH_3)_2NC_6H_4COCHOHC_6H_5$.

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

AN INDIRECT METHOD OF STUDYING THE OXIDATION–REDUCTION POTENTLALS OF UNSTABLE SYSTEMS, INCLUDING THOSE FROM THE PHENOLS AND AMINES

BY LOURS F. FIESER

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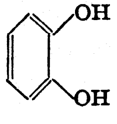
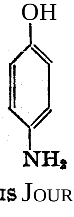
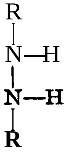
With certain unstable oxidation–reduction systems it has been found possible to measure the potentials with a reasonable degree of accuracy even though decomposition of the oxidant occurs so rapidly that the half-life period is less than one minute.[1] A limit was reached, however, in the application of the method in its present form. Such substances as amphi-naphthoquinone and o-quinone-di-imine decompose so very rapidly that no adequate measurements could be made. The number of such failures of the direct method, to be sure, is comparatively small. In over two hundred cases the simultaneous removal by oxidation of two hydrogen atoms from hydroxyl or amino groups which are ortho or para or adjacent to one another, or which bear some similar relationship, gives rise to a fairly stable oxidant and the system formed by the two components is electromotively active and its potential can be determined by one means or another which involves the direct observation of that potential. The following substances thus belong to what may be termed the "hydroquinone type."







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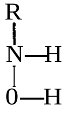
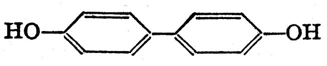


$R-NH-OH$



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[1] Fieser, THIS JOURNAL, 52, 4915 (1930).

On the other hand, there is a second type of compound, to which the monatomic phenols and amines belong, the partial oxidation of which produces an oxidation–reduction system with which a high degree of instability is the rule rather than the exception, for the oxidant is a free radical. Thanks to the brilliant investigations of Wieland, of Pummerer, and of Goldschmidt, the existence of these radicals and the nature of the systems of which they are components is not a question for speculation but one of proof. Since the existence of the diphenyl nitrogen radical was established by Wieland,[2] several bivalent nitrogen radicals[3] and aroxyls[4] have been isolated. Some of these have been obtained by the direct oxidation of the corresponding amine or phenol, and it has been proved in a highly ingenious manner that the primary oxidation product of aniline is a radical containing bivalent nitrogen.[5] With few exceptions the radicals are highly unstable, but the information concerning the nature of their decompositions is very complete. The nitrogen radicals generally polymerize to hydrazines; the aroxyl radical either polymerizes to a peroxide or isomerizes to a keto-methyl radical, which may enter into various subsequent reactions. Careful studies of these reactions have led the workers in this field to conclude that the primary step in the oxidation in neutral medium of all phenols or amines consists in the removal of one hydrogen atom from oxygen or nitrogen.

With respect to the mechanism, then, there is no difference between the oxidation of the monatomic substances and that of the compound of the hydroquinone type. The oxidation products differ to the extent that those of the first class are usually much less stable than those of the second type, but the difference is hardly a significant one, for exceedingly unstable quinones have been described, as well as very stable radicals.

The property most characteristic of the quinones, the azo and similar compounds, is that they respond almost instantly to reduction at a low temperature and in dilute solution. The reverse reaction takes place with equal ease, and it may be said that the hydroquinone–quinone system is an unusually mobile one. No less mobile is the system 9-chloro-10-phenanthrol (I)–9-chloro-10-phenanthroxyl (II).[6]

Possibly because the blocking of the positions ortho and para to the oxygen atom prevents a wandering of the free valence to carbon, and because the high molecular weight retards the velocity of association, the radical,

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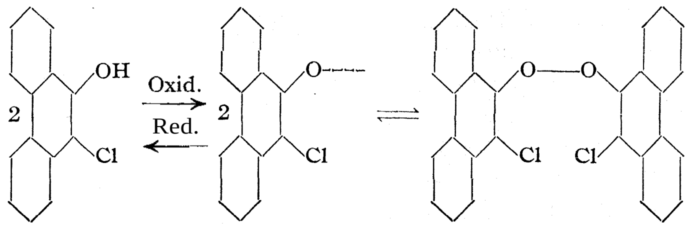
[2] Wieland, *Ann.*, 381, 214 (1911).

[3] See particularly Goldschmidt and collaborators, *Ber.*, 53, 44 (1920); 55, 616, 628 (1922); Ann., 437, 194 (1924).

[4] Pummerer and collaborators, *Ber.*, 47, 1472 (1914); 59, 2161 (1926); Goldschmidt and collaborators, *ibid.*, 55, 3197 (1922); *Ann.*, 438, 202 (1924); 445, 123 (1925); 478, 1 (1930).

[5] Goldschmidt and Wurzschmitt, *Ber.*, 55, 3216 (1922).

[6] Goldschmidt and Steigerwald, *Ann.*, 438, 202 (1924).



I II III

II, is far more stable than the average and in this and other respects it is strikingly similar to the quinones. It does slowly polymerize at ordinary temperatures to the peroxide, III, but Goldschmidt was able to isolate the substance and to characterize it very completely. Outstanding among its properties is the great ease of reduction; the oxidation of I to II may be reversed quantitatively with such reagents as hydrazobenzene, hydroquinone and phenylhydrazine. So great, indeed, is the velocity of reduction of some of the bivalent nitrogen radicals that Goldschmidt and Bader were able to effect a quantitative determination of the radical by titration at $-80°$ with hydrazobenzene solution.[7]

All of the evidence thus shows that there is no essential difference between the systems produced on partial oxidation of compounds of the hydroquinone and of the phenol type, even though the ultimate fate of the oxidant is usually different. It is reasonable to infer that, since the one is electromotively active, the other would share this property, and preliminary experiments with 9-chloro-10-phenanthroxyl have shown that this is the case.' It may even be possible to measure the potentials of such systems, but whether or not a few substances of special structure may be capable of study in this way, it does not seem at all likely that any direct measurements will be possible with compounds such as phenol and aniline. Consequently, we believe that it is worth while to develop an indirect method of study which is entirely general in application, if limited in accuracy.

The Theory of the Method

The general method may be called that of potentiometric indicators and it was originated by Conant.[8] It consists in measuring the potential of a solution of some stable oxidation–reduction system, usually an inorganic one, and then adding a sample of, say, a phenol. If the potential of the solution is so low that the phenol is incapable of becoming oxidized by the oxidant of the system which is being used for reference,

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[7] Goldschmidt and Bader, *Ann.*, 473, 137 (1929).

[8] (a) Conant and Lutz, THIS JOURNAL, 45, 1047 (1923); (h) *ibid.*, 46, 1254 (1924); *(c) ibid.*, 49, 1083 (1927); (d) Conant and Pratt, *ibid.*, 48, 2468 (1926); *(e) ibid.*, 48, 3178 (1926); (f) *ibid.*, 48, 3220 (1926); (g) Conant, Aston and Tongberg, *ibid.*, 52, 407 (1930); (h) Conant, *Chemical Reviews*, **3**, 1 (1926).

no change in the potential of the system will occur; but if the phenol becomes oxidized, it will obviously consume some of the oxidant, and the potential will change and thus indicate that a reaction has proceeded. The experiment can, of course, be made quantitative, so that the decrease in the potential of the inorganic, or "reference system" as we shall call it, indicates the amount of phenol which is oxidized in a given period of time. Now the potential begins to fall at once, but it does not rapidly reach a constant level, as in the interaction of two stable oxidation–reduction systems, but continues to fall at a measurable rate. The reason for this is that the reaction between the two reversible systems, say, those from a-naphthol and potassium ferricyanide (1)

$$\text{ROH} + \text{K}_3\text{Fe(CN)}_6 \rightleftharpoons \text{RO}— + \text{K}_3\text{HFe(CN)}_6 \qquad (1)$$

$$\text{RO}— \longrightarrow \text{Decomposition products} \qquad (2)$$

cannot come to a point of equilibrium because the oxidant of the organic system is unstable and changes over more or less rapidly into other substances according to (2). The destruction of the radical by (2) allows more of it to be formed by (1), and the potential, which is determined by the relative concentrations of the ferri- and ferrocyanides, continues to decrease. The rate at which the potential of the solution decreases is a measure of the rate of Reaction 2, for the first reaction is much more rapid; for practical purposes it may be regarded as instantaneous.

Now Conant has presented evidence in support of the altogether reasonable theoretical conception that the velocity of Reaction *2* is dependent upon the equilibrium constant of Reaction 1. The concentration of the radical available at any instant for Reaction 2 is determined by the extent to which Reaction 1 has proceeded to the right. In other words, the first reaction (rapid) feeds the second (slow). Since the equilibrium constant of Reaction 1 may be expressed in terms of the normal oxidation–reduction potentials and concentrations of the two interacting systems, there is obviously a relationship between the velocity of the decomposition reaction, the potential of the solution, and the normal potential of the arol–aroxyl system. It is desirable to evaluate the last-named quantity, but unfortunately there is one other unknown and undeterminable quantity: the velocity of the un-fed decomposition reaction. For each radical there must be an intrinsic rate of decomposition; the rate which can be measured by the above method is proportional both to this intrinsic rate and to the equilibrium constant of Reaction 1.

If this equilibrium constant is represented in terms of the normal potential of the ferri–ferrocyanidesystem, E_0(Fe), and of the unstable organic system, E_0, the situation may be summed up by means of the equation

$$\textbf{(1)}\quad \text{Observed velocity} = \text{Constant X } \frac{[\text{ROH}][\text{K}_3\text{Fe(CN)}_6]10^{\left(\frac{E_0(\text{Fe}) - E_o}{0.0591}\right)}}{[\text{K}_3\text{H(CN)}_6]}$$

This shows that the velocity of oxidation will be increased by the substitution of another reference system of normal potential greater than E_0(Fe). It is also clear that there are two unknowns, E_0 and the constant which defines the true rate of decomposition of the oxidant.

In order to gain some idea of the potential of the unstable organic system, Conant prepared a series of solutions containing various reference systems so chosen that there was a progression in the potentials of these solutions. A quantity of a given phenol was added to each solution and the potential was followed. Below a certain potential no reaction occurred, above that the potential dropped at a rate which increased as the potential of the solution was increased. By measuring the rates of the reactions and applying certain approximate equations, Conant was able to estimate the potential at which 20–30% of the phenol would be oxidized in the course of thirty minutes; this value he termed the "apparent oxidation potential." The value is dependent upon two factors: the normal oxidation–reduction potential of the phenol–phenoxyl system and the intrinsic rate of decomposition of the phenoxyl radical.

A separation of these two factors is not easily accomplished, but until this is done there can be no adequate means of estimating, even approximately, the true potentials of the unstable systems. To illustrate the point we may quote the example of two substances of the hydroquinone type which form unstable systems on partial oxidation, and for which the potentials, as well as the true velocities of decomposition of the oxidants, have been measured by direct means. The potentials of the systems from *p*-methylaminophenol and from *p*-benzylaminophenol are very nearly identical at PH 3.5 and yet the velocity constant is about seven times as great in the second case as it is in the first.' If the "apparent oxidation potentials" were determined for these substances it would be found, on comparing the action of *p*-methylaminophenol and of *p*-benzylaminophenol on identical solutions of a given reference system, that the drop in potential occurred much more rapidly with the benzyl than with the methyl derivative, and a lower value for the "apparent oxidation potential" would be assigned to this than to the methyl derivative. The "apparent oxidation potentials" would thus indicate a difference between the two systems when there is no appreciable difference in the actual normal potentials.

Thus, even as a means of indicating the relative (true) potentials of a series of closely related compounds, the "apparent oxidation potential" is unreliable. It reflects not only all of the characteristics peculiar to the rate of decomposition of each oxidant, but also the very marked influences on reaction velocities of changes in temperature and environment.

If the facts were otherwise and if the velocity of the reaction were the same for all members of a given series of substances, then Conant's "apparent oxidation potentials" would give an accurate measure of the relative normal potentials of the various systems. Ordinarily, however, the velocities differ considerably. Now it will be observed that the velocity of the reaction is, in part, dependent upon the potential of the reference system and this can be adjusted to progressively lower values and the reaction can thus be made progressively slower and finally brought practically to a stop. Under these conditions the velocities of reaction for a series of compounds all approach the limiting value of zero and hence they are all very nearly the same at some point representing a small percentage of oxidation in a brief period of time. It follows from these considerations that, while the rate factor may influence greatly the "potential at which 20–30% oxidation occurs in thirty minutes," it should have a slight, possibly an inappreciable, effect on the potential at which the velocity becomes vanishingly small.

Critical Oxidation Potentials

We have thus sought to develop a method of determining the potential at which the velocity of the reaction between a given oxidizable substance and a suitable reference system reaches some limiting, small value. We believe that a means of accomplishing this end has been found and that, although the method is of a purely empirical character, it answers to certain reliable tests which may be applied. The method will be described in detail in the Experimental Part; it may be explained here briefly by quoting some experiments with a-naphthol in a neutral 37% alcoholic solution at 25°. The alcohol was included to increase the solvent power; neutral buffer salts were used in order to avoid dissociation phenomena. The potentials given all refer to the difference in potential between the oxidation–reduction electrode and a hydrogen electrode in the same solvent.

The potential of the molybdicyanide–molybdocyanide system may be varied from about 1.0 v. to 1.2 v., but at any potential in this range α-naphthol becomes oxidized with great rapidity. Using the ferri–ferrocyanide system, a rapid oxidation is observed at a potential of 0.870 v., but no reaction can be detected in a reasonable length of time at a potential of 0.770 v. After thus limiting the range to be studied more carefully, a series of solutions of ferri- and ferrocyanides is prepared in such a way that their potentials lie in this range and differ by about 5–10 mv. The total concentration of the cyanides is kept exactly the same, but the ratio of oxidant to reductant is varied. Each solution is brought to thermal and electrochemical equilibrium and the potential is carefully determined. A sample of a-naphthol is then added, the amount taken being just equivalent to the potassium ferricyanide present in each experiment, and the potential is followed for five minutes. At the potentials 0.780 v. and 0.790 v. no oxidation occurs, but at 0.800 v. and above a drop in potential is noted and this becomes progressively greater as the potentials of the solutions increase. There is thus a potential range of 0.790–0.800 v. above which oxidation occurs, below which the extent of the reaction is so limited that no reaction at all can be detected with the apparatus employed. It may be noted that the period of observation may be extended to about thirty minutes and still the reaction fails to become detectable at 0.780 v.

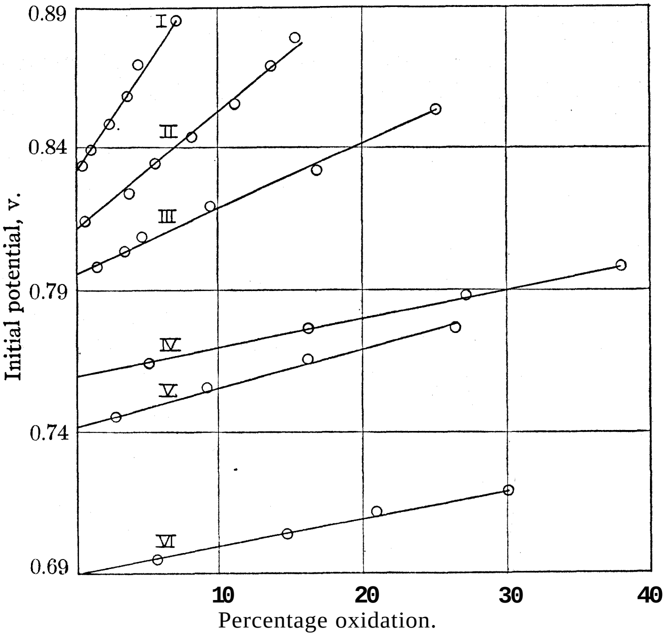

Fig. 1.—The determination of critical oxidation potentials: I, eugenol; II, 2,3-dihydroxy-naphthalene; III, α-naphthol; IV, pyrogallol dimethyl ether; V, catechol; VI, 2,6-dihydroxynaphthalene. Reference systems for I–V, ferro- and ferricyanides; for VI, *p*-hydroxydiphenylamine–N-phenylquinone-imine.

A narrowing of the potential range which thus appears to be critical may be accomplished as follows. The drop in the potential is an indication of the amount of ferricyanide which has entered into reaction and, hence, of the amount of α-naphthol which has been oxidized. One can calculate the percentage oxidation from the equation

$$\text{Percentage oxidation} = 100([\text{Oxid.}]_i - [\text{Oxid.}]_t)/[\text{Oxid.}]_t \qquad (2)$$

where $[\text{Oxid.}]_i$ is the concentration of ferricyanide at the start of the experiment and $[\text{Oxid.}]_t$ is that at time, *t*. These quantities are calculated from the normal potential of the ferri–ferrocyanide system and the potentials at the beginning and end of the experiment, by means of the usual electrode equation. Results of the following nature are obtained (Table I).

Table I

The Oxidation of α-Naphthol

Potential, E(v.)	0.7915	0.7985	0.8040	0.8087	0.8190	0.8321	0.8535
ΔE (mv.)	.0	.9	2.2	3.2	7.3	18.1	38.8
Oxidation, %	.0	1.5	3.4	4.6	9.4	16.8	25.0

While the drop in potential is not directly proportional to the initial potential of the solution, the relationship between the potential and the percentage oxidation is unmistakably linear. These results are represented by Curve III, Fig. 1, and Figs. 1 and 2 give similar graphs for several other compounds. Included in the list are phenols, primary and secondary amines, and compounds of the hydroquinone type (catechol and 2,6-dihydroxy-naphthalene). Two inorganic and one organic reference systems are represented. It is clear that the relationship noted holds good in each case. In fact with over seventy compounds studied it appears to be quite generally true that when equimolecular quantities of the oxidizable substance and the oxidant of a reference system are allowed to interact over a brief period of time, the percentage oxidation is a linear function of the initial potential of the solution.

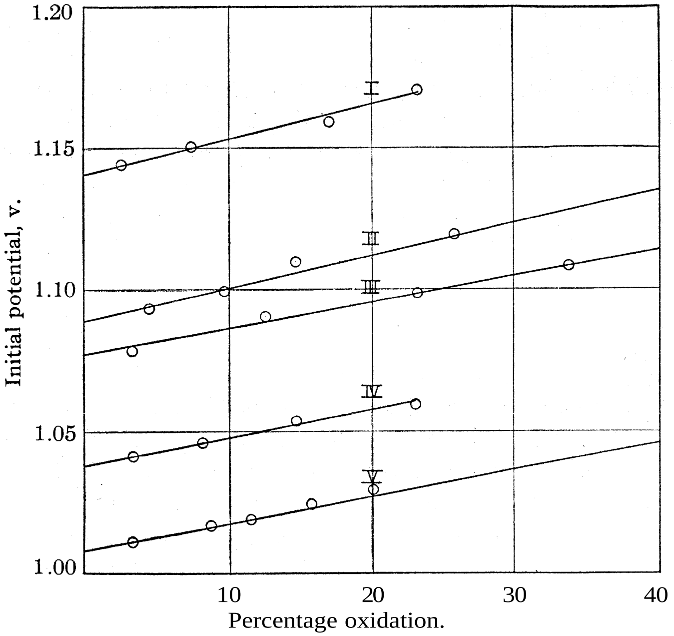

Fig. 2.—The determination of critical oxidation potentials: I, 2-nitro-1-naphthol; II, phenol; III, p-toluidine; IV, p,p'-dihydroxydiphenylmethane; V, diphenylamine. Reference system: cyanides of molybdenum.

We have not been able to solve the complicated problem of deriving this relationship from theoretical principles, but the relationship does exist and use may be made of it in the following way. On extrapolation of the percentage oxidation—potential curve, a potential is obtained which corresponds, on the curve, to the point of "zero oxidation." It really does not correspond to the point at which there is absolutely no reaction but rather to the potential at which the oxidation ceases to be detectable in a short period of time with the particular instruments employed. If these instruments were refined this "zero-oxidation" potential would be shifted to somewhat lower values. Theoretically there is no potential at which the reaction completely comes to a stop. What this extrapolation value does represent is thus the potential at which, with *a* particular technique and apparatus, the rate of the reaction becomes so small as to be just detectable. We shall call this the critical oxidation potential and designate it by the symbol E_c. If it is a reasonably reproducible constant with which to characterize a series of substances, it is evident that this critical oxidation potential meets precisely the requirements defined above, for it is a constant determined both by the potential-factor and the rate-factor, but for which, since the rate is made very small, the rate-factor must be exceedingly small.

The accuracy with which the critical oxidation potential can be determined may be judged from the following results. Two series of experiments with a-naphthol both gave the value **0.796** v. When the concentrations of all of the reactants were halved, the value obtained was **0.799** v. In a further series another reference system having a different normal potential was employed; with the complex cyanides of tungsten the E_c value found was **0.798** v. The percentage oxidation–potential curve in this case had a slightly different slope. It is probable that catalysts would also change the slope of the curve without changing the point of origin.

The only limitation discovered in the application of this method is that there are not enough suitable reference systems to cover the entire range of potential. The potentials of the systems which we have used are represented in Fig. **3.** The most satisfactory results are obtainable when the potential desired can be secured without resorting to either very high or very low values for the ratio of oxidant to reductant. It will be seen that this can be done in the lower potential zone, for the curves for four systems overlap each other. There is a range, however, between the systems from tungsten and molybdenum which cannot be covered. The upper and lower limits of the usefulness of these systems are indicated on the graph; critical oxidation potentials falling between **0.91** v. and **1.01** v. cannot be determined until other systems of suitable potential are discovered.

The slopes of the potential–oxidation curves vary over wide limits, indicating quite different reaction velocities. This difference probably is not entirely due to the nature of the unstable substances produced on oxidation, for there is a general disposition for the curves to become steeper as the relative amount of the oxidant of the reference system is increased. Thus Curves I–V of Fig. 1 all refer to experiments in which the complex cyanides of iron were employed, and the ratio of ferri- to ferrocyanide varied from values of about 4–5 for Curve I, to 0.1–0.3 for Curve V. The slopes of the curves seem to reflect this variation.

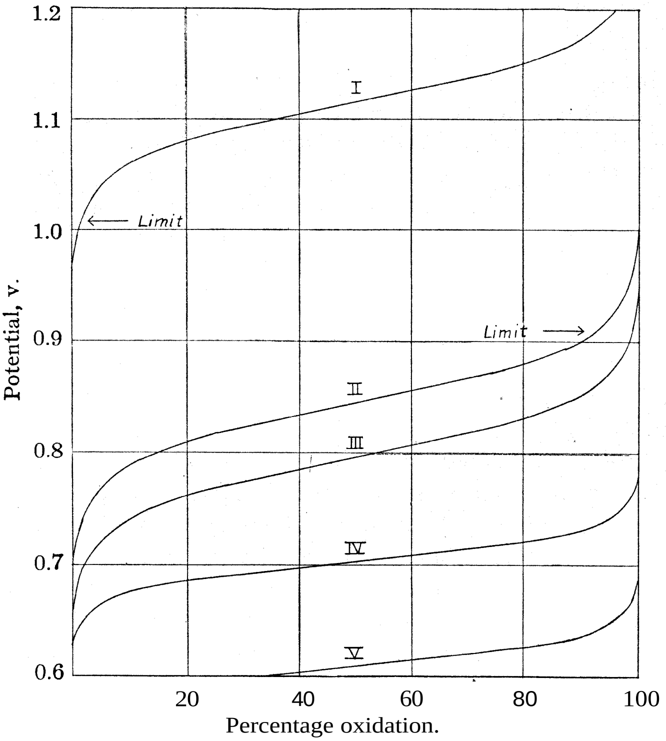

Fig. 3.—The potentials of the reference systems: systems. named as reductant, I, potassium molybdocyanide; II, potassium tungstocyanide; III, potassium ferrocyanide; IV, *p*-hydroxydiphenylamine; V, 2,4-diaminodiphenylamine.

Tests of the Reliability of the New Constant.—According to the reasoning developed above, the critical potentials which have been determined should bear some definite relationship to the normal oxidation–reduction potentials of the unstable systems to which they refer. For a group of similar substances the critical potentials would be expected to lie at some approximately constant distance below the normal potential. We have been fortunate enough to find a few systems for which both of these potentials may be determined, and the results are summarized in Table II. The determinations were all made in a neutral phosphate buffer solution containing 37% of alcohol. The potentials are those measured against a hydrogen electrode in the same solvent. The compounds listed are all of the hydroquinone type (two hydrogens involved).

TABLE II

THE RELATIONSHIP BETWEEN THE NORMAL OXIDATION–REDUCTION POTENTIAL (E_0) AND THE CRITICAL OXIDATION POTENTIAL (E_c)

System, named as reductant	$E_0{}^1$, v.	E_c, v.	Difference, v.
p,p'-Dihydroxydiphenyl	0.954	0.882	0.072
p,p'-Dihydroxystilbene	.854	.786	.068
p-Phenylenediamine	.783	.710	.073
p-Aminophenol	.733	.673	.060
		Av.	.068

Although these results are not very extensive, they do indicate a constant difference between the two potentials. The variation in the difference is no greater than the uncertainty in the experimental results. The decomposition of two of the oxidants here concerned is a monomolecular reaction; with the other two it is a catalytic second-order reaction. The half-life periods vary from sixty seconds to 234 seconds.[1] When these great differences are considered, it seems quite clear that the rate-factor has been reduced to a minimum in the new term which has been called the critical oxidation potential.

Where direct determinations of normal potentials have not yet been possible it appears admissible to estimate approximate values from the critical potential values and the average difference found up to the present time for similar systems, that is, for systems of the same oxidizing equivalence. Table III gives values calculated in this manner for all of the compounds of the hydroquinone type which have been studied.[9] The normal potential for o-benzoquinone has been measured[10] in alcoholic hydrochloric acid solution by a method which very probably yields low results; the value found was 0.784 v.

TABLE III

NORMAL POTENTIALS (CALCD.) AT 25° IN NEUTRAL ALCOHOLIC SOLUTION

System, named as oxidant	E_0, v.
o-Benzoquinone	0.810
Amphi-naphthoquinone	.758
Nitro-p-benzoquinone	.765
3-Hydroxy-1,2-benzoquinone	.677
Isatin	.813
Quinone from aesculetin	.827

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[9] A more accurate estimate would be obtained by taking the mean of the critical oxidation potential of the reductant and the critical reduction potential of the oxidant if the latter quantity could be evaluated.

[10] Conant and Fieser, THIS JOURNAL, 46, 1858 (1924).

Another test of the soundness of considering the critical oxidation potential as a potential-factor from which the rate-factor has been very nearly separated is in determining the effect of temperature. One valuable feature of this test is that it may be applied to each compound individually, rather than to a series. The few measurenients which we have made at 40° are not as accurate as those at 25°, but they will serve to show the order of magnitude of the effect of this variable. The results are described in the Experimental Part and summarized in Table IV. A 15° increase in the temperature has relatively little effect on the critical oxidation potential; this quantity decreases by from 3 to 21 mv. The direction of the change and its magnitude are entirely comparable with the change in the normal oxidation–reduction potentials of the quinones.[11]

TABLE IV

THE EFFECT OF TEMPERATURE

Compound	Critical oxidation potential, E_c, v. 25°	40°	Difference
4-Nitro-1-naphthol	...	1 123	...
2-Nitro-1-naphthol	1 141	1 120	-0 021
2,4,6-Trichlorophenol	1 103	1 097	006
1-Naphthol-2-carboxylic acid	1 065	1 062	003
Hydroquinone monomethyl ether	0 848	0 833	.015
2,3-Dihydroxynaphthalene	812	809	003
a-Naphthol	797	784	013
Phloroglucinol	799	791	008
p,p'-Dihydroxystilbene	786	.773	.017
1,3-Dihydroxynaphthalene	754	744	010

The effect of a temperature change is thus that normal to true potentials. Where a rate-factor is involved as in Conant's "apparent oxidation potentials," it has been found[S] that a 37° increase in temperature causes a decrease in the "potential" of as much as 150–400 mv.

One other standard by which the critical potential may be judged is that of the consistency of the results, and we shall now attempt to determine whether the figures obtained reveal any regularities and form a consistent pattern.

The Relationship between Critical Oxidation Potentials **and** Structure.—The values found for the critical oxidation potentials at 25° are recorded in Table XIII of the Experimental Part. From these figures tables have been constructed which will simplify the comparisons. The first of these, Table V, shows the effect produced on the critical potential of phenol and of α-naphthol of substituting various groups in the ortho, para or meta position to the hydroxyl group. The influence of a given group is very nearly the same for ortho or para substitution, that of a meta group is in the same direction but only 16–18% as great, and this is true whether the potential is increased or decreased.

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[11] Conant and Fieser, THIS JOURNAL, 44,2480 (1922).

TABLE V

A COMPARISON OR ISOMERIDES

Substituent	Substance	Effect of substituent on E_c of substance Ortho	Para	Meta
Methyl	Phenol	−0.049	−0.050	−0.009
Phenyl	Phenol	.041	.043	...
Methoxyl	Phenol	.221	.241	.037
Nitro	a-Naphthol	.336	.339	...

Table VI gives a comparison of the oxidation of the hydroxyl and the amino group when attached to an aromatic nucleus. It is seen that the amines become oxidized only at a higher potential than that required for the corresponding phenols. The difference is so nearly constant that one could make a fairly accurate estimate of the potential of an amine from a knowledge of the potential of a phenol of similar structure.

TABLE VI

A COMPARISON OF PHENOLS AND AMINES

Amines	E_c, v.	Phenols	E_c, v.	Difference
Aniline	1.135	Phenol	1.089	0.046
p-Toluidine	1.077	*p*-Cresol	1.039	.038
p-Anisidine	0.892	*p*-Methoxyphenol	0.848	.044
p-Naphthylamine	1.064	8-Naphthol	1.017	.047

In constructing Table VII, which summarizes the data on the influence of substituent groups, we have regarded ortho and para substitution to be identical, and we have considered and combined the results in the phenol and in the amine series. The figure representing the effect of the nitro group should be accepted with some reservation. A comparison of a substituted with an unsubstituted compound, in this case 2-nitro-1-naphthol with α-naphthol, is only valid when the hydroxyl group is un-ionized in each case. It is not unlikely that the nitro derivative is ionized to some extent in the buffer solution employed; hence the observed difference which we have attributed to the nitro group represents only the order of magnitude of the true effect.

TABLE VII

THE EFFECT (v.) ON THE CRITICAL OXIDATION POTENTIAL OF ORTHO OR PARA SUBSTITUENTS

Group	Effect	Group	Effect
$—NO_2$	0.344	$—CH_2CH{=}CH_2$	−0.037
—COOH	.268	$—CH_2COOH$	− .038
—CHO	.212	$—C_6H_5$	− .042
$—SO_3H$	.084	$—CH_3$	− .052
—Cl	.005	$—OC_6H_5$	− .059
$—CH_2OH$	− .037	$—OCH_3$	− .235
$—CH_2C_6H_5$	− .037	$—N(CH_3)_2$	− .371

In general, unsaturated groups increase the potential, saturated ones decrease it; the nitro group has the greatest positive effect, the modified hydroxyl and amino groups the greatest effect in the negative direction. Ortho–para directing groups usually weaken the bond holding the hydrogen atom to oxygen or nitrogen, meta directing groups have the opposite effect.

When the few results for polysubstituted substances are 'considered, it is found that the influence of a given group increases as the number of such groups in the molecule is increased. The effect of a meta hydroxy group may be estimated in two ways: phenol may be compared with resorcinol; α-naphthol may be compared with 1,3-dihydroxynaphthalene. The differences found in E_c are 0.046 v. and 0.043 v., respectively. A comparison of resorcinol with phloroglucinol, on the other hand, indicates that the introduction of one more meta hydroxyl group lowers the potential 0.244 v. Other substituents usually behave in the same fashion. We do not yet know how to account for this increased effect with increasing substitution, but the same thing was observed among the oxidation–reduction potentials of substituted phenanthrenequinones.[12]

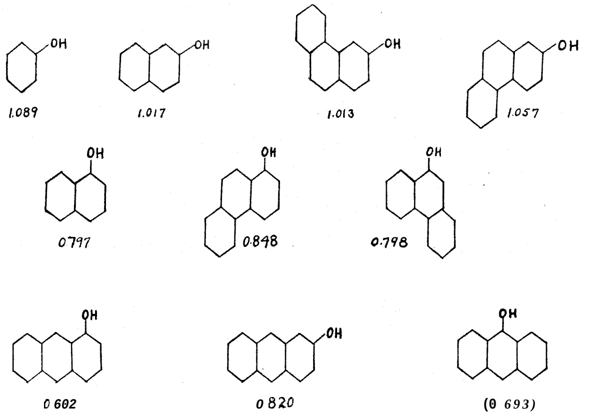

Fig. 4.—Critical oxidation potentials of phenols.

The next comparison is of the phenols derived from the various aromatic hydrocarbons, and the data are recorded in Fig. 4. According to the potentials, the substances fall into definite groups. The four phenols at the top differ relatively little in potential; they are structurally similar in that the oxidizable group is either in the unreactive 8-position to a second benzene ring, or else no such ring is present. This may be called the β-naphthol type. The second group consists of **α-naphthol, 1-phenanthrol** and 9-phenanthrol, and their potentials are all nearly 0.2 v. lower than those of the compounds of the β-naphthol type. In each of these three substances the hydroxyl group is adjacent to a benzene ring, which

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[12] Fieser, This Journal, 51, 3101 (1929).

is thus in a position to exert an activating influence. In these two series the nature of the hydrocarbon skeleton appears to be of little consequence and the dominating influence is that which may be exerted by an adjacent aromatic nucleus.

In the last line are to be found results for three anthracene derivations. On account of the uncertainty introduced by its extensive ketonization, the value for anthranol is not reliable. The figures for α- and β-anthrol clearly show that neither compound fits into the a- or β-naphthol series. It will be observed, however, that each is lower in potential than the corresponding naphthalene derivative by almost exactly the same amount, 0.195 v. for the a-derivative and 0.197 v. for β-anthrol. The difference between the *a*- and β-positions of anthracene is thus the normal one, but in this case the hydrocarbon structure appears to have a specific activating influence which is quite appreciable. This influence may be related to the other unique properties of anthracene.

Another interesting comparison is that given in Table VIII, which gives the potentials for a few secondary amines which result from the replacement of one of the amino hydrogen atoms of aniline by various groups. Alkyl groups cause a rather slight lowering of the potential, indicating that they tend to weaken the nitrogen–hydrogen linkage; the unsaturated phenyl group has an effect which is similar but greater, while the presence of a carbon–nitrogen double bond adjacent to the oxidizable group appears to produce a very marked change in the potential. In view of this fact, it appears odd that the azo group of diazoaminobenzene has such a moderate influence.

TABLE VIII

THE EFFECT OF N-SUBSTITUTION ON THE CRITICAL OXIDATION POTENTIAL OF ANILINE

Subst.	$C_6H_5N{=}N—$	$C_6H_5CH_2—$	$CH_3—$	$C_2H_5—$	$C_6H_5—$	$C_6H_5CH{=}N—$
Effect, v.	−0.077	−0.078	−0.082	−0.097	−0.127	−0.344

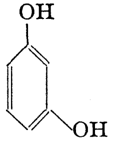
Some Theoretical Speculations

It is evident that, on the whole, the critical oxidation potentials of a large number of substances reveal many regularities and reasonable relationships; the constant responds just as well to this criterion of reliability as it does to specific experimental tests. We thus feel confident that this new constant gives a dependable, if approximate, indication of the relative normal potentials of the compounds concerned and that it may be taken as a true measure of the tendency of a given substance to become oxidized. Because of this demonstrated reliability, we shall now venture to present a few deductions of a somewhat speculative nature.

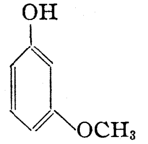
1. The Possibility of Quinone Formation.—The property of forming a quinone on oxidation is not shared by all dihydroxyl derivatives of the aromatic hydrocarbons, and it is important to determine the requirements

for this type of reaction and the limitations. Whether or not 2,3-dihydroxynaphthalene possesses this property is a question which has received considerable attention and one to which some of the present results may be applied, for the ability of a substance to yield a quinone, azo compound or similar oxidant, rather than a univalent radical, appears to be reflected in the potential.

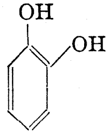
With resorcinol (IV) the formation of a quinone is impossible and the relation of the potential to that of phenol gives a measure of the effect of one meta hydroxyl group. The potential of the monomethyl ether, V, gives a measure of the influence of a meta methoxyl, and it will be observed that the effect is practically the same for these two groups. Turning to the ortho derivatives, catechol (VI) would be expected to have a potential very close to that of guaiacol (VII) if the oxidation involved a single hydrogen atom and the formation of a univalent radical. The observed potential, however, is very much below that of guaiacol, and the obvious reason for this is that the oxidation of catechol is different and results in the formation of a quinone. Even the transitory existence of the most unstable of quinones should affect the potential in this way.



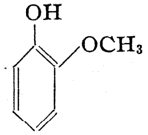
E_c = 1.043 v.
IV



E_c = 1.052 v.
V

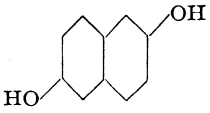


E_c = 0.742 v.
VI

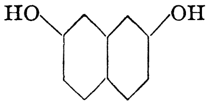


E_c = 0.868 v.
VII

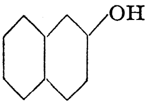
A further example of the manner of applying this criterion of quinone formation is the case of the oxidation of 2,6-dihydroxynaphthalene (VIII). If this substance is to be imagined as a 8-naphthol derivative which will become oxidized at a single hydroxyl group, we need a means of predicting the effect on this oxidation of the hydroxyl in the second nucleus. A comparison of 2,7-dihydroxynaphthalene (IX) with 8-naphthol (X) indicates that this effect ordinarily is practically negligible. The potential of VIII, however, is not at all close to that of 8-naphthol, but far below it. This may be interpreted as the result of the formation on oxidation of the highly unstable *amphi*-naphthoquinone.



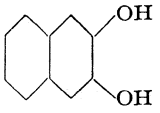
E_c = 0.690 v.
VIII



E_c = 1.007 v.
IX



E_c = 1.017 v.
X

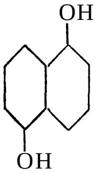


E_c = 0.812 v.
XI

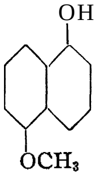
The possible existence of "2,3-naphthoquinone" may now be considered. The oxidation potential of 2,3-dihydroxynaphthalene (XI) is only 0.205 v.

below that of β-naphthol (X). It has been shown that the effect of a hydroxyl group is about the same as that of a methoxyl, where the oxidation is of the univalent type, and it is known that the effect on the potential of phenol of an ortho-methoxyl group is 0.221 v. The value is so close to the difference between X and XI that a completely adequate conception of the potential of XI is given by the assumption that the oxidation is of the univalent type, that it is simply an ortho substituted naphthol which cannot form a quinone.

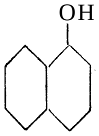
The opposite decision is reached in the case of 1,5-dihydroxy-naphthalene (XII). A comparison of the ether, XIII, with a-naphthol (XIV) indicates that a methoxyl in the 5-position, and hence by inference a hydroxyl in that position, has little effect upon the potential for the oxidation at the single hydroxyl group in the 1-position. Since the potential of 1,5-dihydroxynaphthalene is 0.124 v. below that of a-naphthol, it must be concluded that the oxidation is not similar to that of α-naphthol and that a quinone is formed, however brief its existence.



E_0 = 0.673 v.
XII

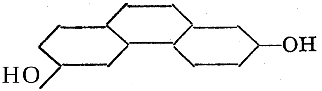


E_0 = 0.792 v.
XIII

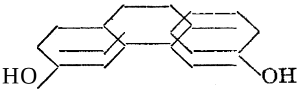


E_0 = 0.797 v.
XIV

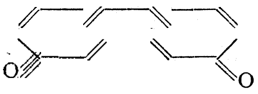
In the phenanthrene series it is found that an hydroxyl group in one terminal ring has little influence on the potential of oxidation at an hydroxyl in the other terminal nucleus. The 2,6-dihydroxy derivative (XV) is to be regarded as a substituted 3-phenanthrol, and its potential is practically identical with that of this compound. On the other hand, the potential of the 3,6-derivative (XVI) is well below that for its isomer and this suggests that the quinone, XVII, is the primary oxidation product. Preliminary qualitative tests with 3,6-dihydroxyphenanthrene have failed to reveal any indication of the formation of a quinone,[13] but this problem will now bear closer study.



E_0 = 1.010 v.
XV



E_0 = 0.832
XVI



XVII

2. The Nature of the Compounds of the Hydroquinone Type.—Some comparison of the systems involving one and those involving two hydrogens in the oxidation process has been made above in a qualitative way,

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[13] Fieser, THIS JOURNAL, 51, 2480 (1929).

but when a closer relationship between the two types is desired, the critical oxidation potentials do not furnish an adequate basis for comparison. This can only be obtained through a knowledge of the normal potentials and the free energies of the oxidation.

It has been shown that for a few substances of the hydroquinone type it is possible to relate the critical potential (E_c) to the normal potential (E_0) experimentally. On the average, the former is 0.068 v. below the latter. From the electrode equation, which must apply to E_c as well as to any potential of the system, one may write

$$E_c - E_0 = -0.068 = 0.02957 \log [\text{Oxid.}]/[\text{Red.}] \quad (3)$$

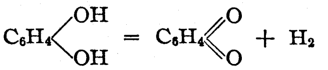
A calculation from this equation shows that the potential represented by E_c corresponds to a point at which 0.5 part of the oxidant is in equilibrium with 99.5 parts of the reductant; in other words, we have determined in *E*, the potential at which 0.5% of the reductant becomes oxidized in five minutes. Though the amount is quite small, it appears that this represents quite closely the extent of the reaction in each case.

The difference, $E_c - E_0$, was determined for systems with which two hydrogens are removed on oxidation, hence the difference would not be the same where a monatomic phenol or amine is concerned. In the latter case the equation becomes

$$E_c - E_0 = 0.05915 \log [\text{Oxid.}]/[\text{Red.}] \quad (4)$$

The experiments, however, establish that the reaction proceeds to the extent of 0.5% in five minutes. We have shown that the variation in the rate of the reaction is insignificant when the rate is so very small and we are thus justified in assuming that the extent of oxidation would be very nearly the same for all similar systems. Since there is an abundance of evidence to show that the hydroquinone–quinone and arol–aroxyl systems are entirely similar, we may assume 0.5% reaction for the latter system and thus calculate from Equation 4 that the difference between E_c and E_0 is 0.136 v. We regard this value, which gives a means of estimating the normal potentials for the systems containing radicals, *as* uncertain only to the extent that it is an approximation which may be subject to some revision as more data accumulate.

Having a method of estimating approximate values for the normal potentials, the free energy changes in the oxidations can be calculated. Thus for phenol the critical potential is 1.089 v., hence the normal potential for the phenol–phenoxyl system is 1.089 + 0.136 = 1.225 v. The normal potential for the quinone–hydroquinone system is 0.715 v. The free energy changes are as follows



$$C_6H_4{<}^{OH}_{OH} = C_6H_4{<}^{O}_{O} + H_2$$

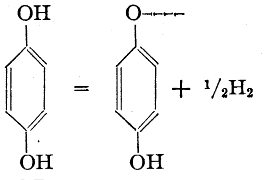
AF = 33.0 Cal.

$$C_6H_5OH = C_6H_5O\text{---} + {}^1/_2H_2$$

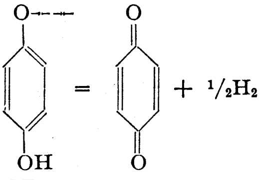
AF = 28.3 Cal.

Not much more energy is required for the removal of two hydrogens from hydroquinone than for the oxidation of the single hydrogen of phenol.

One interesting application of these calculated free energy changes is to the question of the possibility of carrying out the step-wise oxidation of hydroquinone. Estimates of the free energy changes for the removal of each hydrogen atom may be made in the following way. Considering the first step in the reaction, hydroquinone may be regarded as a substituted phenol which is converted into a univalent radical. The hypothetical critical potential for this oxidation would be close to that of its monomethyl ether (E_c = 0.848 v.), and one can estimate from the known relationship between hydroxy and methoxy compounds (resorcinol and its ether) that the value would be 0.839 v. The normal potential would be 0.136 v. greater, or 0.975 v., and the increase in free energy 22.5 Cal. For the complete oxidation of hydroquinone to quinone the energy change is 33.0 Cal. The difference between these quantities gives the free energy change in the second step of the process. We may thus write



AF = 22.5 Cal.



AF = 10.5 Cal.

This shows that considerably less energy is required for the removal of the second hydrogen atom than for the first. If the energy level in a given oxidation experiment is great enough to produce the radical, it will be more than sufficient to complete the oxidation. The free radical is thermodynamically unstable except when it is present at very low concentrations. If it were possible to prepare it by some other method, it would disproportionate to give quinone and hydroquinone. The situation may be expressed in terms of the equilibrium constants of the two reactions (3×10^{-17} and 2×10^{-8}), and it may be shown that the concentration of the radical in a solution containing 0.1 M each of quinone and hydroquinone is 4×10^{-6}.

By following similar processes of reasoning we have estimated the corresponding free energy changes for other substances which yield quinones, and the figures are given in Table IX.

TABLE IX

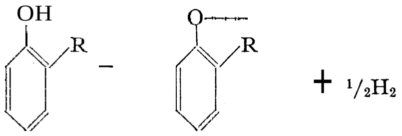
CALCULATED FREE ENERGY CHANGES IN THE OXIDATION OF HYDROQUINONES

	AF, Cal.	
Reductant	First hydrogen	Second hydrogen
Hydroquinone	22.5	10.5
Catechol	23.0	14.4
2,6-Dihydroxynaphthalene	26.4	8.6
p,p'-Dihydroxydiphenyl	27.0	17.0

Invariably the energy required to complete the oxidation of the radical is very much less than that required to produce it. This not only serves to explain why radicals or their reaction products (other than quinones) have never been observed in the oxidation of this type of compound, but it also gives a new insight into the nature of these substances. When one hydrogen atom has been separated from the hydroxylic oxygen atom, the free valence on this oxygen transmits to an ortho or para hydroxyl or amine group a reactivity, a mobility, which it did not before possess.

3. The Effect of Substituents on the **Normal** Potentials of the **Quinones.**—Throughout the entire investigation of the subject named it has been a perplexing problem to decide whether the observed shifting in the normal potential of an oxidation–reduction system as the result of the introduction of a substituent group, or of other structural change, is to be regarded as connected with the structural change in the oxidant or in the reductant. Thus the normal potential of the quinone-hydroquinone system is lowered 0.121 v. by the introduction of a methoxyl group;[14] but there has been no way of telling whether this pronounced change results from the fact that the methoxyl group weakens the oxygen–hydrogen bond of the hydroxyl groups of hydroquinone, or if it is because of an effect of this group on the unsaturated system of quinone, causing the molecule to have a diminished tendency to add hydrogen in the 1,6-positions. Possibly both factors are of importance. On account of the great contrast in the structure of the oxidant and reductant, oxidation cannot be visualized as the exact reverse of reduction. This is, however, true of the oxidation of a phenol to a free radical, for each substance retains the truly aromatic structure and it is immaterial whether one considers the activation of the functional hydrogen atom of the reductant or the affinity of the univalent oxygen atom of the oxidant for hydrogen.

One may compare guaiacol with phenol and thus obtain a difference in the free energy changes which represents the effect of the methoxyl group



$-\Delta F$ (Cal.) $\begin{cases} R = H: & 28.3 \\ R = OCH_3: & 23.2 \end{cases}$

Difference = 5.1

The effect of the methoxyl group in guaiacol, which is thus determined, must be very nearly the same as the effect of that group on the hydroxyl group ortho to it in methoxyhydroquinone. The influence of the substituent on the second hydroxyl group cannot be very great, because this group is in the meta position and groups which are meta to each other have very little effect on one another. A comparison of the hydroquinone system with the methoxy-substituted system gives the following results

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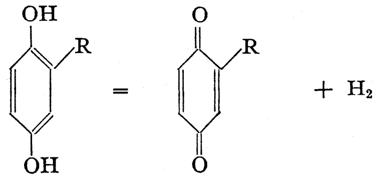
[14] The value for the normal potential of methoxyquinone (0.594 v.) was **kindly** supplied by Dr. J. B. Conant.



$$-\Delta F\ (\text{Cal.}) \begin{cases} R = H: & 33.0 \\ R = OCH_3: & 27.4 \end{cases}$$

Difference = 5.6

The effect of substitution is hardly any greater than that found above for guaiacol, and this means that almost the entire change brought about by introducing this group is to be attributed to the influence of that group on the character of the hydroquinone, and that the change produced in the quinone molecule is relatively insignificant.

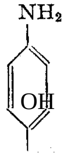
The inference which the present results suggest, namely, that the normal potential of a quinone–hydroquinone system is influenced much more by the change produced in the reductant as the result of substitution than by the corresponding change in the oxidant, is an important one and one which will be investigated further.

While the effect of simple substitution now appears traceable largely to the character of the hydroquinone in question, there can be no doubt that the influence of some structural changes must be attributed to the nature of the quinone in question. Thus, for example, the pronounced difference in the normal potentials of the quinone–hydroquinone and the o-benzoquinone–catechol systems results from a difference inherent in the two quinones and not in their reduction products, for there is good evidence that ortho and para substitution produce the same effect on the oxidation potential of a phenol.

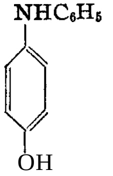
4. The Relationship between Various Oxidizable Substances.—With the information supplied by the present study of phenols and amines, we are in a position to understand somewhat better the relationship between the various types of compounds which yield more or less stable oxidation products by the loss of two hydrogen atoms.

Since a given primary amine is oxidized only at a potential higher than that required for the oxidation of the corresponding phenol, we may conclude that the hydrogen is the more firmly bound in the primary amino group. This gives a rational explanation of the fact that the normal potential of the hydroquinone–quinone system is progressively increased by the substitution of amino and imino groups for the hydroxyl and ke-

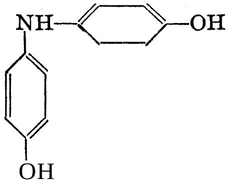
E_0 = 0.715 v.
XVIII



E_0 = 0.733 v.
XIX



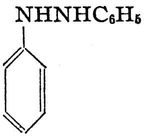
E_0 = 0.703 v.
XX



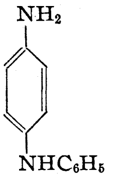
E_0 = 0.656 v.
XXI

tone groups, respectively (Compare XVIII and XIX).[1] That diphenylamine is lower in potential than aniline accounts for the relationship between XIX and XX. The structural difference between XX and XXI is that the latter substance has one additional para hydroxyl group. Since such a group has been found to impart a considerable mobility to a hydroxylic or amino hydrogen, the shifting of the potential of the system of which XXI is the reductant to a lower level is easily understood. Thus the systems from the quinones, the quinone-imines and di-imines, the quinone-anils, the indophenols and indamines are all closely related to one another and in a qualitative way their relative potentials are now understood.

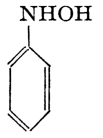
On considering the structures of hydrazobenzene and phenylhydroxylamine, which form systems with azobenzene and nitrosobenzene, respectively, one is impressed by the relationship of these substances to *p*-aminodiphenylamine and to *p*-aminophenol. The first two compounds



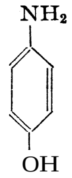
E_0 = 0.420 v.[15]
XXII



E_0 = 0.751 v.
XXIII



E_0 = 0.562 v.
XXIV



E_0 = 0.727 v.
XXV

are amines in which there is, adjacent to the amino group, a group which appears to impart a considerable reactivity to the amino hydrogen. Once this hydrogen has been removed by oxidation, the resulting free valence in turn aids in the immediate oxidation of the group which caused the activation. The other two substances, XXIII and XXV, are exactly similar except that their activating group which eventually becomes oxidized is across the benzene ring from the first group, rather than adjacent to it. One may roughly estimate how the activating effect of a group would compare when it is in these two situations by considering the critical potentials of aniline (1.135 v.), N-methylaniline (1.053 v.) and *p*-toluidine (1.077 v.). Attaching the methyl group to nitrogen, and substituting it in the para position, both cause a lowering in the potential but the effect of N-substitution is the greater of the two. Consequently it is understandable that the potentials for hydrazobenzene and phenyl hydroxylamine are lower than those for their isomers.

5. A Possible Reason for Certain Molecular Rearrangements.—The comparisons which have just been made suggest an interesting relationship in the field of the molecular rearrangements. This can be made

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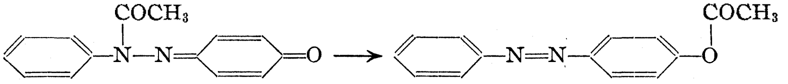
[15] This value is estimated from the potentials for 3,3′-diaminoazobenzene (0.4095 v.) and azobenzene-4,4′-disulfonate (0.424 v.). Compare: Biilmann and Blom, *J. Chem. Soc.*, 125, 1719 (1924); Conant and Pratt, Ref. 8d.

clear by the following statements. Under certain conditions N-methylaniline (E, = 1.053 v.) can be caused to rearrange into *p*-toluidine (E_c = 1.077 v.); phenylhydroxylamine (E_0 = 0.562 v.) yields p-aminophenol (E_0 = 0.733 v.); the hydrazobenzenes (hydrazobenzene, E_0 = 0.420 v.) rearrange either to benzidines (benzidine, E_0 = 0.921 v.[16]), or semidines (p-aminodiphenylamine, E_0 = 0.751 v.). In each case the rearrangement involves the formation of a less oxidizable isomer, a substance of higher potential. The converse of this proposition appears equally true as, for example, in the case of the rearrangement of acetylquinonephenylhydrazone, XXVI, into acetoxy-azobenzene, XXVII. From the known potentials for quinone-imines and for azo compounds it is quite safe to assume that the azo compound has the lower reduction potential, so that the change represented here is from one reducible substance to an isomer which is less reducible. This reaction constitutes one of the few exceptions to Latimer's theory of molecular rearrangements,[17] and yet it falls into line with the other reactions noted. It has been shown that a given reducible substance tends to tautomerize, if this is possible, into a less reducible form, a form of lower reduction potential.[18] There is a suggestion in the present observations that a given reducible (or oxidizable) substance possesses a tendency to rearrange, where possible, into an isomeric form which is less reducible (or oxidizable).


XXVI XXVII

Experimental Part

Buffer Solution.—The solvent employed in all of the experiments was 0.038 M in potassium dihydrogen phosphate and 0.067 M in disodium hydrogen phosphate, and contained approximately 37% of alcohol. It was prepared by diluting 534 cc. of a solution 0.07 M in potassium dihydrogen phosphate and 0.105 M in disodium hydrogen phosphate to a volume of 1 liter with 95% alcohol. When diluted with water instead of alcohol, the solution had a P_H value of 7.04. The alcoholic solution contains about the maximum quantity of salts, and crystallization is likely to occur if it is allowed to stand for any length of time at a temperature below 25°.

Potassium Molybdocyanide, $K_4Mo(CN)_8 \cdot 2H_2O$.—After carrying out several preparations of this material according to the method outlined by Rosenheim,[19] the following procedure was adopted as being rapid and reliable.

One hundred grams of molybdic acid (85% MoO_3) and 210 cc. of concentrated hydrochloric acid were added to a solution of 210 g. of sodium thiocyanate in 1.2 liters of water and the mixture was boiled under the reflux condenser for three hours. The deep red solution of the basic molybdenum-IV-thiocyanate was filtered by suction and

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[16] Clark, Cohen and Gibbs, Supplement No. 54 to *Pub. Health Repts.* (1926).

[17] Latimer, THIS JOURNAL, 51, 3185 (1929).

[18] Fieser, *ibid.*, 50, 439 (1928).

[19] Rosenheim, *Z. anorg. Chem.*, **54**, 97 (1907); see also, *ibid.*, **49**, 149 (1906).

60 cc. of pyridine was added slowly to the well-stirred solution. A dark red oil was thus precipitated, and toward the end of the addition a light yellow solid began to separate. On thorough cooling in an ice-bath the red oil solidified (dry weight, 148 g.). Without drying the product or breaking up the lumps the pyridine compound was stirred into a solution of 300 g. of potassium cyanide in 500 cc. of water. Noxious gases were evolved and the material rapidly dissolved to give a solution which was first green and then yellow-brown, The mixture was heated on the steam-bath and stirred for one-half hour, filtered from a certain amount of black material, and evaporated on the water-bath until a large crop of amber-colored crystals had separated. After cooling, the material was collected and washed with a small amount of potassium chloride solution. The crystals collected in this way were usually contaminated with a considerable amount of black material, but the latter is not soluble in water and is easily removed. The crude product was dissolved in warm water, the solution was treated with animal charcoal, filtered, and to it there was added one to two volumes of alcohol. The potassium molybdocyanide soon separated in the form of golden-yellow crystals of great purity; yield, 100 g. Further evaporations of the cyanide mother liquor yielded, after two or three recrystallizations, 9 g. more of the pure product.

Potassium Molybdicyanide Solution, $K_3Mo(CN)_8$.—Oxidation to the pentavalent cyanide was carried out according to Olsson.[20] A solution of 4.4 g. of potassium molybdocyanide in 20 cc. of water and 10 cc. of 6 N sulfuric acid was titrated with a 10% solution of potassium permanganate until a pink color indicated complete oxidation. Fifty cc. of 10% silver nitrate solution was then added to precipitate the molybdicyanide in the form of the fine, brown-red silver salt. This was collected on a Biichner funnel washed with water, suspended in 50–100 cc. of water, and treated with 50 cc. of 10% potassium chloride solution. By shaking the mixture vigorously in a stoppered flask the silver salt was soon decomposed. The solution was filtered by suction from the silver chloride, clarified with animal charcoal and diluted to a volume of 250 cc. As the pentavalent molybdenum compounds are sensitive to light, the above operations were carried out in the dark-room.

The strength of the molybdicyanide solution was determined by electrometric titration with potassium ferrocyanide, and it was found to vary from 0.032 to 0.034 M. The solution was diluted to 0.030 M and stored in the dark. The fresh solution always contained a small amount of molybdocyanide, as revealed by the titration curve, and when exposed to the light of the laboratory the concentration of molybdicyanide decreased at the rate of about 0.2% per hour.

Potassium Ferricyanide and Ferrocyanide Solution.—These solutions were prepared by dissolving 0.03 mole of the salt in 200 cc of water and diluting to 1 liter with the alcoholic buffer solution. The solutions decompose slowly and should be rejected after the second day.

Procedure for the Determination of Critical Oxidation Potentials.—The five reversible oxidation–reduction systems which were employed as reference systems are listed in Table X. Since the potentials of the complex cyanides vary considerably with dilution, it was essential to determine the normal potential under conditions comparable with those of the oxidation tests. For this purpose 20 cc. of the 0.03 M potassium ferrocyanide solution was added to 200 cc. of the buffer solution and titrated electrometrically with 0.03 M molybdicyanide solution, giving a curve from which the normal potential could be calculated. The potential of

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[20] Qlsson, Ber., 47, 917 (1914).

TABLE X

NORMAL POTENTIALS OF THE REFERENCE SYSTEMS

0.0016 N solution of oxidant and reductant in neutral alcoholic phosphate solution

System, named as reductant	Abbreviation	E_0 25°	E_0 40°
Potassium molybdocyanide	Mo	1.1160	1.111
Potassium tungstocyanide	W	0.8450	0.833
Potassium ferrocyanide	Fe	.7965	.786
p-Hydroxydiphenylamine	A	.7030	..
2,4-Diaminodiphenylamine	B	.6090	..

the oxidation–reduction half-cell was measured against a hydrogen electrode immersed in some of the same solvent, and the value found when [Oxid.] = [Red.] is that reported as the normal potential. In the case of potassium tungstocyanide, a solution of 0.0006 M of the salt in 20 cc. of water was added to 200 cc. of the buffer solution and titrated with potassium molybdicyanide, while 0.0003 M of each of the organic compounds was dissolved in 220 cc. of the solution and titrated with the same reagent. The potential of the molybdicyanide–molybdocyanide solution was determined by titration of the oxidant with ferrocyanide solution and correcting the titration curve for a small amount of the reductant which was invariably present.

The molybdenum system reaches a constant potential with great rapidity while such constancy is reached relatively slowly in the case of *p*-hydroxydiphenylamine and, when the proportion of the reductant is small, with the complex cyanides of iron. Solutions of 2,4-diaminodiphenylamine should be protected from the air, for the rate of oxidation is sufficient to cause trouble.

The potentials recorded in the table are all subject to a slight inaccuracy owing to the fact that it was necessary to prepare the 0.03 M complex cyanide solutions either with water (Mo, W) or with a mixture of water and buffer solution (Fe), rather than with the latter solution alone.

In performing the oxidation tests the solutions were prepared in exactly the same manner, and with the same amounts and concentrations, as in these determinations of the normal potentials, but the titration was discontinued when the desired potential had been reached. The relationship between the potential of the system and the ratio of oxidant to reductant is conveniently expressed in the form of a large graph showing the potential plotted against Equivalents of oxidant $\times 10^5$. When completely oxidized, each solution contains 6×10^{-4} equivalent of the oxidant, and the curves may be constructed from the normal potentials given and the theoretical equations. Having titrated a solution to the potential desired, the number of equivalents of oxidant present was found by reference to the chart and the equivalent amount of the substance to be studied was dissolved in 30 cc. of the buffer solution. While releasing the stop watch, this solution was poured through a funnel into the oxidation–reduction vessel (three seconds required for the addition) and the potential was recorded after one minute and after five minutes. When a progressive drop in potential occurred, the extent of the reaction after five minutes was determined from the potential at that time and the chart.

It was usually necessary to apply a correction to the potentials actually noted after adding the sample under investigation. In most cases it was observed that at potentials well below that at which oxidation quite evidently occurred, the potential dropped almost immediately about 1 mv. and then remained constant indefinitely. Such a drop in potential can hardly be indicative of an oxidation, for such a reaction is not instantaneous and proceeds at a regular rate. As will be shown later, the potential is decreased to a certain extent as the result of diluting the solution of the reference system by the addition of the sample, but this does not account for the entire effect. It is probable that a further factor is the change in the activities of the oxidant and reductant produced by the organic material added. A correction for the effect was applied in the following manner. With each substance studied experiments were carried out at such a potential that this small change in potential during the first minute to a constant value could be observed, that is, at a potential 5–10 mv. below that fixed for E_c. This change in potential was then subtracted from the initial potential of the solution in each of **the** other experiments with the compound in question, for the same drop, which is not due to oxidation, must occur in each case. In calculating the percentage oxidation these corrected potentials were employed. The correction was greatest with the molybdenum system, amounting usually to about 2 mv., and it was scarcely perceptible with the organic systems.

The Use of Various Reference Systems and the Effect of Changing the Concentrations.—The procedure may be illustrated by quoting in full the measurements with a-naphthol at 25°. In Series I, Table XI, the first two experiments show that the potential of the ferri–ferrocyanide system falls 1 mv. on adding one equivalent of α-naphthol and then remains constant. In the next experiment the potential might be expected to fall 1 mv. whether or not a reaction occurs; the corrected initial potential is thus 0.7985 v. But the potential falls progressively, hence .a reaction occurs at this potential level. From the corrected initial potential and the potential at the five-minute interval it was calculated that 1.5% of a-naphthol was oxidized during this period of time. On plotting the corrected initial potentials against the percentage oxidation for the entire series, a value of 0.796 v. was found for the critical oxidation potential. It should be noted that the second and third experiments **fix** this value as between 0.7930 v. and 0.7990 v. and that the remaining experiments serve merely to give a means of interpolating accurately be-

TABLE XI

DETERMINATION OF THE CRITICAL OXIDATION POTENTIAL OF α-NAPHTHOL (25°)

	Potential of reference system, v.				
	Initial	Initial (corr.)	1 Min.	5 Min.	% oxidation
	0.7864	0.7854	0.7854	0.7854	0.0
	.7940	.7930	,7930	.7930	.0
Series I	.8000	.7990	.7990	.7980	1.6
System: Fe	.8113	.8103	.8100	.8070	4.7
	.8210	.8200	.8185	.8120	9.9
	.8321	.8311	.8260	.8150	15.0
	E_c = 0.796 v.				
Series II. Duplicate of I.	E_c = 0.796 v				
	0.7915	0.7905	0.7905	0.7905	0.0
	.8052	.8042	.8041	.8037	2.8
Series III	.8132	.8122	.8115	.8105	5.2
System: W	.8214	.8204	.8198	.8167	10.8
	.8273	.8263	.8236	.8200	16.8
	.8306	.8296	.8283	.8222	18.2
	E_c = 0.798 v.				
Series IV	0.7913	0.7913	0.7913	0.7913	0.0
System: Fe	.8057	.8057	.8053	.8040	2.3
	.8156	.8156	.8147	.8113	5.8
Using one-half the usual quantities of oxidant and of a-naphthol	.8192	.8192	.8178	.8116	9.4
	.8233	.8233	.8218	.8143	10.2
	.8328	.8328	.8295	.8174	13.2
	.8515	.8515	.8330	.8160	23.3
	E_c = 0.799 v.				

tween these figures. The second series of experiments is that referred to in the first part of this paper. In connection with Series III it may be pointed out that the normal potential of the tungsten system differs considerably from that of iron, which means that the amount of oxidant present at a given potential was less than half that used in Series I. In spite of this difference, the percentage oxidation at a given potential was only slightly greater and very nearly the same result was obtained for E_c. Series IV shows that halving the concentrations of both the oxidant and the a-naphthol does not materially alter the value for E_c or the percentage oxidation at a given potential,

In deciding upon a time interval at which to compose the extent of oxidation at different potentials it was felt that, aside from the theoretical considerations which have been mentioned earlier, this interval should be fairly short in order to avoid secondary oxidations and in order that the potential of the reference system should not fall so far as to diminish greatly the initial driving force of the reaction. Comparison of the results for the one-minute and the five-minute intervals showed that the latter were much more consistent and regular, and this period of time was thus adopted for all of the experiments at 25°.

The Effect of Varying the Ratio of Oxidant to Substance Oxidized.—In each of the experiments just described the amount of a-naphthol taken was that equivalent to the oxidant of the reference system. Since there is no theoretical reason for preferring this particular ratio, experiments were undertaken to determine the effect of varying the ratio indicated. Table XII summarizes the critical oxidation potentials found for six compounds under different conditions of concentration. Each figure represents the results of extrapolating a curve constructed from the results of five or six experiments similar to those described above. The total amount of the reference system was kept the same (0.0006 mole), and the amount of the sample was varied in each series in the proportions shown in the Table. Though the results are not recorded in detail, it may be said that it was invariably found that as the proportion of the sample to the oxidant was increased, the percentage oxidation at a given potential above the critical potential became progressively less. That is, a greater percentage of the sample was oxidized in five minutes when the total amount of substance was small than when a large excess was present.

TABLE XII

CRITICAL OXIDATION POTENTIALS (25°)

Compound	Reference system	E_c (v.) when equiv. ratio of oxidant to sample was 1:05	1:1	1:2	1:3	1:4
Aniline	Mo	1.137	1.135	1.121	1.116	...
p-Toluidine	Mo	1.080	1.077	1.063	1.059	...
p-Cresol	Mo	...	1.038	1.023	...	1.021
β-Naphthol	Mo	...	1.016	1.006	...	...
Aesculetin	Fe	...	0.766	0.759	...	...
Catechol	Fe	...	.754	.742	0.739	...

The results show that E_c decreases as the relative amount of phenol or amine is increased. This is in accord with the prediction from the electrode potential equation. The greatest difference seems to occur between the results for the 1:1 and the 1:2 ratios, though the difference appears to be fairly constant (av., 12 mv.) for all six compounds and to be independent of the nature or the potential of the reference system. The results in themselves furnish no basis for preferring any particular set of conditions for carrying out a large number of determinations, and considerations of a practical nature governed the choice. Several of the compounds which it seemed desirable to study are so sparingly soluble in the buffer solution employed that it would not be possible to adopt the concentrations called for by the higher ratios. Thus in all subsequent evaluations of critical potentials the 1:1 ratio was adopted.

General Application of the Method.—On the basis of the orienting experiments which have been described, the following general procedure was adopted as being that most suitable for a wide survey of oxidizable substances. A solution of 0.0006 equivalent of the completely oxidized or reduced form of the reference system in 220 cc. of the alcoholic buffer solution (or in a mixture of 200 cc. of this solution and 20 cc. of water) was titrated to the potential desired with a suitable reagent. The substance to be studied in amount equivalent to the oxidant present, and dissolved in 30 cc. of buffer solution, was added, the percentage oxidation at five minutes was determined and the critical potential found in the usual way.

In studying ortho or para dihydroxy or diamino compounds, and substances of similar structure, it was assumed that the primary oxidation is of the 2-hydrogen type. Thus for each mole of a complex metal cyanide one-half mole was taken of catechol, pyrogallol, *p*-phenylenediamine, 1,5- and 2,6-dihydroxynaphthalene, *p,p'*-dihydroxystilbene, *p*-hydroxyphenylglycine and similar substances. The percentage oxidation in these cases was calculated on the basis of the assumption made.

A complete record of the experiments will not be given, but rather a summary of the significant results. In Table XIII, under the symbol E, there is given for each compound the initial potentials of the reference system, corrected for the drop observed when no progressive reaction occurred, and the corresponding percentages of oxidation observed in five minutes ("% Oxid."). The correction applied ("Corr.") and the critical oxidation potential, E_c, follow these figures. In the one or two cases in which it was not possible to determine the magnitude of the correction term, this was estimated from the behavior of similar compounds under similar conditions.

Though experiments quoted above indicate that about the same amount of α-naphthol is oxidized at a given potential by either potassium ferricyanide or potassium tungsticyanide, there is little assurance that this would be true in every case, and thus it was considered advisable to use a single reference system in determining the potential for each substance studied. The nature of the reference system employed is indicated in the heading of each small table, using the abbreviations listed in Table X.

The majority of the compounds studied are simple substances which are easily obtainable in a state of purity. Many of them, purchased from the firms of Kahlbaum, Schuchardt and Eastman, required no further purification. A few of the compounds have been described in recent publications of the author, others were supplied by the E. I. du Pont de Nemours & Company, while some were prepared according to known methods. In each case the sample was purified until it corresponded to the literature description of the pure material, and it does not appear necessary to record the physical constants. While the present method of determining oxidation potentials makes some use of the velocity of oxidation, it is very improbable that catalysts would appreciably influence the results. It is conceivable that one sample of a phenol might contain a catalyst which would accelerate the oxidation and that the slope of the percentage oxidation–potential curve would be different from that obtained with the pure compound, but the extrapolations to the point of zero oxidation should give very nearly the same results in each case.

TABLE XIII

CRITICAL OXIDATION POTENTIALS AT 25°

I. PHENOLS

Phenol

E, Mo, v.	% oxid.
1 0875	0.0
1 0935	4.5
1 0995	9 7
1 1098	14.6
1.1192	25.8
1.1375	42.0

Corr. = 1.5
E, = 1.089 v.

o-Cresol

E, Mo, v.	% oxid.
1.0313	0.0
1.0420	2.7
1 0469	9 4
1.0541	14.5
1.0586	23.3

Corr. = 1.4
E, = 1.040 v.

p-Cresol

E, Mo, v.	% oxid.
1.0293	0.0
1.0400	3.8
1 0465	11.3
1.0531	24.2
1.0593	38.6

Corr. = 2.0
E_c = 1.038 v

m-Cresol

E, Mo, v.	% oxid.
1.0765	0.0
1.0867	7.3
1.0927	13.5
1.0985	19.8
1.1083	32.8

Corr. = 1.5 **mv.**
E_c = 1.080 v.

2,4-Dimethylphenol

E, W, v.	% oxid.
0.8877	0.0
.9023	0.8
.9135	1.9
.9255	3.2

Corr. = 2.5 **mv.**
E, = 0.895 v.

p-Hydroxyphenylacetic acid

E, Mo, v.	% oxid.
1.0467	0.0
1.0452	3.9
1.0570	7.2
1.0667	12.5
1.0707	20.6
1.0770	29.5

Corr. = 1.3 **mv.**
E_c = 1.051 v.

p-Hydroxydiphenyl-**methane**

E, Mo, v.	% oxid.
1 0466	0.0
1 0537	2.4
1 0572	3.4
1 0620	11.2
1 0734	19.8

Corr. = 1.8 mv.
E_c = 1.052 v.

p,p'-Dihydroxydi-**phenylmethane**

E, Mo, v.	% oxid.
1.0278	0.0
1.0414	3.3
1.0460	8.1
1.0534	14.6
1.0593	23.0
1.0673	47.5

Corr. = **2.2** mv.
E_c = 1.038 v.

Saligenin

E, Mo, v.	% oxid.
1.0512	0.0
1.0582	3.2
1.0660	5.0
1.0720	**9.2**
1.0812	10.8

Corr. = 1.5 mv.
E_c = 1.052 v.

o-Hydroxydiphenyl

E, Mo, v.	% oxid.
1.0256	0 0
1.0378	1.7
1.0426	3.8
1.0478	4.9

p-Hydroxydiphenyl

E, Mo, v.	% oxid.
1.0214	0.0
1.0368	4.0
1.0415	6.1
1.0470	12.5

Guaiacol

E, Fe, v.	% oxid.
0.8588	0.0
.8684	.1
.8748	.2
.8780	.5

TABLE XIII (*Continued*)

E, Mo, v.	% oxid.
1.0556	15.2
1.0660	34.0

Corr. = 1.9 mv.
E_c = 1.038 v.

E, Mo, v.	% oxid.
1.0520	23.5
1.0570	37.9

Corr. = 2.0 mv.
E_c = 1.036 v.

E, Fe, v.	% oxid.
.8848	.9

Corr. = 1.2 mv.
E_c = 0.868 v.

Hydroquinone monomethyl ether

E, Fe, v.	% oxid.
0.8400	0.0
.8507	.4
.8561	.7
.8630	1.5
.8738	2.6

Corr. = 1.7 mv.
E_c = 0.848 v.

Resorcinol monomethyl ether

E, Mo, v.	% oxid.
1.0380	0.0
1.0555	1.5
1.0593	4.8
1.0622	6.6
1.0695	9.5
1.0787	11.8

Corr. = 2.0 mv.
E_c = 1.052 v.

Pyrogallol dimethyl ether

E, Fe, v.	% oxid.
0.7510	0.0
.7643	5.1
.7765	16.2
.7883	27.1
.7780	38.0

Corr. = 1.2 mv.
E_c = 0.760 v.

p-Hydroxydiphenyl ether

E, Mo, v.	% oxid.
1.0040	2.0
1.0108	10.0
1.0143	11.1
1.0185	23.6
1.0258	29.4
1.0363	46.4

Corr. = 1.7 v.
E_c = 1.030 v.

Cresol

E, Fe, v.	% oxid.
0.8198	0.0
.8311	.9
.8398	2.2
.8501	3.7
.8598	5.1

Corr. = 1.2 mv.
E_c = 0.825 v.

Eugenol

E, Fe, v.	% oxid.
0.7905	0.0
.8343	.4
.8398	1.0
.8485	2.3(5)
.8585	3.6
.8698	5.3
.8863	7.0

Corr. = 0.7 mv.
E_c = .831 v.

Isoeugenol

E, Fe, v.	% oxid.
0.7535	0.0
.7600	5.7
.7700	13.8
.7790	25.1
.7900	34.6

Corr. = 0.5 mv.
E, = .757 v.

m-Aminophenol

E, W, v.	% oxid.
0.8917	0.0
.9037	.5
.9142	.8
.9245	1.1

Corr. = 2.3 mv.
E_c = 0.894 v.

p-Dimethylaminophenol

E, A, v.	% oxid
0.7123	0.0
.7230	1.7
.7273	6.0
.7310	7.1
.7400	8.9

Corr. = 3.5 mv.
E_c = 0.718 v.

2,4,6-Trichlorophenol

E, Mo, v.	% oxid.
1.1000	0.0
1.1103	6.9
1.1191	9.5
1.1293	20.9
1.1390	30.2

Corr. = 1.7 mv.
E_c = 1.103 v.

Vanillin

E, Mo, v.	% oxid.
1.0778	0.0
1.0878	12.7
1.0985	32.7
1.1071	48.8
1.1247	65.5

Corr. = 2.2 mv.
E_c = 1.080~.

Catechol

E, Fe, v.	% oxid.
0.7277	0.0
.7454	2.7
.7554	9.2
.7654	16.2
.7754	24.6

Corr. = 0.6 mv.
E_c = .742 v.

TABLE XIII *(Continued)*

Resorcinol

E, Mo, v.	% oxid.
1.0160	0.0
1.0460	2.8
1.0471	4.0
1.0515	8.8
1.0565	12.9
1.0659	28.8
1.0790	46.6

Corr. = 2.0 mv.
E_c = 1.043 v.

Nitro-hydroquinone

E, A, v.	% oxid.
0.6935	0.0
,7020	5.2
.7110	10.1
.7222	12.4
.7297	19.7
.7380	22.0

Corr. = 0.0
E_c = .697 v.

Aesculetin

E, Fe, v.	% oxid.
0.7554	0.0
.7622	3.2
.7698	6.1
.7797	12.6
.7940	26.7

Corr. = 0.3 mv.
E_c = .759 v.

Phloroglucinol

E, Fe, v.	% oxid.
0.7980	0.0
.8207	2.5
.8330	3.5
.8520	4.6
.8624	5.5
.8745	7.0

Corr. = 1.0 mv.
E_c = 0.799 v.

Pyrogallol

E, B, v.	% oxid.
0.6052	0.0
.6132	3.1
.6188	6.8
.6235	12.9
.6313	16.6

Corr. = 0.0 mv.
E_c = .609 v.

II. NAPHTHOLS

β-Naphthol

E, Mo, v.	% oxid.
0 9935	0.0
1.0167	1.4
1.0208	3.5
1.0240	5.4
1.0275	11.4
1.0370	18.5

Corr. = 1.5 mv.
E_c = 1.017 v.

2-Nitro-1-naphthol

E, Mo, v.	% oxid.
1.1285	0 0
1.1442	2 6
1.1505	7.4
1.1597	17.0
1.1708	23 2

Corr. = 1.8 mv.
E_c = 1.141 v.

1-Naphthol-2-carboxylic acid

E, Mo, v.	% oxid.
1.0570	0.0
1.0692	5.5
1.0728	8.0
1.0820	19.6
1 0917	27.0

Corr. = 2.0 mv.
E_c = 1.065 v.

Sodium 1-naphthol-2-sulfonate

E, W, v.	% oxid.
08765	0.0
,8875	0.7
.8933	1 3
.9017	2.2
.9113	3.4

Corr. = 2.5 mv.
E_c = 0.881 v.

5-Methoxy-1-naphthol

E, Fe, v.	% oxid.
0.7800	0.0
.7960	1.5
.7990	2 9
.8070	6.7
.8118	9.1
.8142	11.0

Corr. = 1.0 mv.
E_c = 0.792 v.

1,3-Dihydroxy-naphthalene

E, Fe, v.	% oxid.
0.7480	0.0
.7592	5.4
.7692	12.7
.7790	23.3
.7980	38.4

Corr. = 1.0 mv.
E_c = 0.754 v.

1,5-Dihydroxy-naphthalene

E, A, v.	% oxid.
0 6650	0.0
.6763	4.5
.6835	14.1
.6876	22.6
.6955	34.4
.7030	46.3

Corr. 0.0
E_c = 0.673 v.

2,3-Dihydroxynaphthalene

E, Fe, v.	% oxid.
0.7965	0.0
.8140	.7

2,6-Dihydroxynaphthalene

E, A, v.	% oxid.
0.6860	0.0
.6950	5.7

2.7-Dihydroxynaphthalene

E, Mo, v.	% oxid.
1.0065	6.1
1.0145	7.0

TABLE XIII (*Continued*)

E, Fe, v.	% oxid.	E, A, v.	% oxid.	E, Mo, v.	% oxid.
.8240	3.7	.7040	14.8	1.0202	13.4
.8343	5.5	.7120	21.0	1.0249	23.9
.8438	8.1	.719	30.0	1.0302	30.7
.8558	11.2				
.8690	13.7				
.8787	15.3				
Corr. =	0.9 mv.	Corr. =	0.0	Corr. =	1.5 mv.
E_0 =	.812 v.	E_0 =	.690 v.	E_0 =	1.007 v.

III. ANTHROLS

Anthranol (anthrone)		α-Anthrol		β-Anthrol	
E, A, v.	% oxid.	E, B, v.	% oxid.	E, Fe, v.	% oxid.
0.6878	0.0	0.6036	2.5	0.8143	0.0
.6982	10.5	.6098	9.1	.8240	3.2
.7058	26.8	.6145	15.2	.8316	4.8
.7085	41.0	.6220	18.8	.8365	7.2
		.6255	22.4	.8472	14.4
Corr. =	0.0	Corr. =	0.0	Corr. =	1.0 mv.
E_0 =	.693 v.	E_0 =	.602 v.	E_0 =	0.820 v.

IV. PHENANTHROLS

1-Phenanthrol		2-Phenanthrol		3-Phenanthrol	
E, Fe, v.	% oxid.	E, Mo, v.	% oxid.	E, Mo, v.	% oxid.
0.8438	0.0	1.0494	0.0	1.0145	3.6
.8563	.9	1.0584	1.7	1.0195	8.0
.8675	1.8	1.0659	8.6	1.0250	21.2
.8896	4.1	1.0612	10.2	1.0310	23.4
		1.0707	10.5		
		1.0769	29.6		
Corr. =	0.9 mv.	Corr. =	2.3 mv.	Corr. =	2.0 mv.
E_0 =	.848 v.	E_0 =	1.057 v.	E_0 =	1.013 v.

9-Phenanthrol		2,6-Dihydroxyphenanthrene		3.6-Dihydroxyphenanthrene	
E, Fe, v.	% oxid.	E, Mo, v.	% oxid.	E, Fe, v.	% oxid.
0.7945	0.0	1.0000	0.0	0.8224	0.0
.8026	2.0	1.0123	6.3	.8321	.4
.8101	2.6	1.0178	9.7	.8412	2.7
.8196	6.3	1.0247	22.4	.8521	5.0
.8265	7.4	1.0315	34.7	.8654	8.1
.8331	10.9				
Corr. =	0.7 mv.	Corr. =	2.0 mv.	Corr. =	1.3 mv.
E_0 =	.798 v.	E, =	1.010 v.	E_0 =	0.832 v.

V. OTHER HYDROXY COMPOUNDS

p,p'-Dihydroxydiphenyl		*p,p'*-Dihydroxystilbene		Dioxindole	
E, W, v.	% oxid.	E, Fe, v.	% oxid.	E, Fe, v.	% oxid.
0.8778	0.0	0.7712	0.0	0.7330	0.0
.8921	1.6	.7940	5.4	.7465	.6
.9069	2.7	.7987	6.0	.7566	2.7

TABLE XIII (*Continued*)

E, W, v.	% oxid.	E, Pe, v.	% oxid.	E, Fe, v.	% oxid.
.9221	3.7	.8103	13.9	.7695	6.5
		.8223	21.2	.7773	8 0
		.8355	25.4		

Corr. = 2.4 mv.
E, = 0.882 v.

Corr. = 1.0 mv.
E_0 = 0.786 v.

Corr. = 2.0 mv.
E_0 = 0.745 v.

VI. AMINES

Aniline

E, Mo, v.	% oxid.
1.1282	0.0
1.1387	2.3
1.1472	3.6
1.1525	5.3
1.1650	11.5

Corr. = 1.8 mv.
E_0 = 1.135 v.

N-Methylaniline

E, Mo, v.	% oxid.
1.0430	0.0
1.0578	3.0
1.0627	7.0
1.0680	11.4
1.0778	25.0

Corr. = 2.0 mv.
E_0 = 1.053 v.

N-Ethylaniline

E, Mo, v.	% odd.
1.0366	0.0
1.0431	2.3
1 0484	4.0
1.0576	5.6
1.0678	7.2
1.0784	16.5

Corr. = 1.6 mv.
E_0 = 1.038 v.

N-Benzylaniline

E, Mo, v.	% oxid.
1.0520	0.0
1.0556	1.4
1.0646	4.3
1.0708	5.4
1.0759	6.3
1.0831	8.4
1.0886	15.2

Corr. = 1.4 mv.
E_0 = 1.057 v.

Diphenylamine

E, Mo, v.	% oxid.
1.0042	0.0
1.0116	3.3
1.0170	8.7
1.0189	11.3
1.0246	15.7
1.0294	20.0
1.0492	45.2

Corr. = 1.8 mv.
E_0 = 1.008 v.

p,p'-Diethoxydiphenylamine

E, Fe, v.	% oxid.
0.8284	0.0
.8396	.5
.8533	3.7
.8645	5.7
.8770	8.0
.8906	10.6

Corr. = 0.9 mv.
E_0 = .836 v.

p-Toluidine

E, Mo, v.	% oxid.
1.0636	0.0
1.0785	3.3
1.0903	12.5
1.0986	23.1
1.1083	33.8
1.1148	41.3

Corr. = 1.7 mv.
E_0 = 1.077 v.

p-Anisidine

E, W, v.	% oxid.
0.8898	0.0
.9001	.5
.9098	.8
.9308	1.5

Corr. = 2.4 mv.
E, = 0.892 v.

m-Toluylenediamine

E, Fe, v.	% oxid.
0.8580	0.0
.8685	.3
.8772	.6
.8872	1.5

Corr. = 2.0 mv.
E_0 = 0.864 v.

Benzalphenylhydrazine

E, Fe, v.	% oxid.
0.7883	0.0
.7938	1.4
.7981	5.6
.8083	9.6
.8211	13.0

Corr. = 1.7 mv.
E_0 = 0.791 v.

Diazoaminobenzene

E, Mo, v.	% oxid.
1.0562	0.0
1.0642	8.1
1.0682	12.0
1.0772	21.6
1.0924	43.2

Corr. = 1.3 mv.
E_0 = 1.058 v.

Phenylglycine

E, Fe, v.	% oxid.
0.7976	0.0
.8350	.7
.8452	2.1
.8557	3.3
.8645	3.9
.8867	5.5

Corr. = 0.0
E_0 = .833 v.

β-Naphthylamine

E, Mo, v.	% oxid.
1.0552	0.0
1.0696	8.7
1.0794	17.2
1.0889	31.6
1.0962	45.0

Corr. = 1.8 mv.
E_0 = 1.064 v.

TABLE XIII (Concluded)

VII. AMINOPHENOLS AND PHENYLENEDIAMINES (ORTHO AND PARA)

p-Aminophenol		*p*-Phenylenediamine		*p*-Amino-diphenylamine		*p*-Hydroxy-phenylglycine	
E, A, v.	% oxid.	E, A, v.	% oxid.	E, A, v.	% oxid.	E, B, v.	% oxid.
0.6587	0.0	0.7093	0.0	0.6950	0.0	0.6000	0.0
.6765	4.5	.7113	3.8	.7010	1.8	.6060	2.9
.6818	5.3	.7150	5.0	.7075	3.2	.6107	6.3
.6920	11.7	.7220	8.3	.7115	8.7	.6155	10.1
.7070	14.6	.7308	12.2	.7205	9.8	.6255	18.9
.7395	28.8	.7428	13.2	.7330	11.3		
Corr. = 0.0		Corr. = 0.7 mv.		Corr. = 0.0		Corr. = 1.0 mv.	
E_c = .673 v.		E_c = .710		E_c = .696 v.		E_c = 0.603 v.	

VIII. THIOPHENOLS AND MERCAPTANS

n-Propyl mercaptan		Isopropyl mercaptan		Mercapto-benzothiazole	
E, Fe, v.	% oxid.	E, Fe, v.	% oxid.	E. Fe, v.	% oxid.
0.8125	0.0	0.8197	0.0	0.7839	0.0
.8190	.9	.8299	1.2	.7928	3.2
.8250	1.9	.8431	1.5	.8105	5.0
.8335	2.0	.8528	1.6	.8200	5.7
.8430	3.7	.8672	1.9	.8335	5.3
.8525				.8487	6.0
1.0900 (Mo)	49 0				
Corr. = 1.0 mv.		Corr. = 0.6 mv.		Corr. = 0.5 mv.	
E_c = 0.812 v.		E_c = .819 v.		E_c = .785 v.	

While no special effort was made to exclude all traces of catalytically active impurities, it was absolutely essential to free the sample of more easily oxidizable substances. Thus preliminary experiments with commercial samples of the monomethyl ethers of the dihydroxybenzenes gave irregular results which were very probably due to the presence of a small amount of unmethylated material. When this was removed by extracting the ethereal solution of the substance with water, and then distilling and crystallizing the product, no irregularity was noted.

Measurements at 40°.—At the beginning of this research we hoped to provide for the study of even very sparingly soluble substances, and with this end in view the early procedure called for a relatively small volume (100 cc.) of buffer solution as solvent for the reference system (in 20 cc.), while the sample was dissolved in 130 cc. of the buffer.

A temperature of 40° was chosen in order to further increase the amount of material which could be accommodated. It was observed, however, that the potential of the molybdenum system often dropped as much as 15 mv. even when no progressive reaction occurred, and blank determinations soon showed that the drop in potential is largely the result of dilution. The potential of the molybdenum system was found to become less positive by about 12 mv. when the volume was increased from 120 cc. to 250 cc., and the change was independent of the ratio of oxidant to reductant. Since the ratio of the concentrations of the two components of the system is not influenced by dilution, the observed change in potential must be the result of a change in the ratio of their activities, and the direction of the effect is such as to indicate that the activity coefficient of the reductant increases more rapidly with dilution than that of the oxidant. The same was true of the ferri–ferrocyanide system, though the effect was less pronounced. The decrease in potential on dilution ranged from 1.5 mv. to 7.5 mv. as the ratio of oxidant to reductant varied from $^1/_9$ to 9.

When determinations of critical oxidation potentials were carried out it was found that the rapid decrease in potential to a constant value, which was observed at a region well below that at which a progressive reaction occurred, was always somewhat greater than that attributable solely to dilution. The components of the system thus appear to be affected by the oxidizable substance even when no oxidation occurs. While no means of eliminating this effect was found, the effect of dilution was reduced to a minimum in the determinations which have been described above. The original procedure was thus soon abandoned, for the large correction term which had to be applied to the initial potentials rendered the results subject to an unnecessary source of error. The few determinations which had been made before the method was modified have been summarized in Table IV of the Theoretical Part.

It should be stated that when working at 40° the velocity of oxidation is much greater than at the lower temperature. Consequently the time interval over which the fall in potential of the reference system was observed was made shorter, namely one minute instead of five minutes. The reference systems used were those of iron, molybdenum and tungsten, and their potentials at 40° are recorded in Table X.

Normal Oxidation–Reduction Potentials of Stable Systems.—In the course of this survey of oxidizable substances a constant watch was kept for electromotively active oxidation–reduction systems of sufficient stability to permit direct potentiometric study. Such a system may reveal itself in the determination of the critical oxidation potential by causing a very rapid drop in potential to a constant value. A few such cases were discovered, and it was found that the reductant could be titrated in the ordinary way with molybdicyanide. Sharp, reproducible potentials were established in the mixtures of the oxidant and reductant and there was no drift in potential which would indicate a destruction of the oxidant. A summary of the results for this group of substances is given in Table XIV, and two more compounds of this type have been listed in Table X. The figures represent the averages of several closely agreeing determinations. The solutions of the amines (0.0003 mole in 220 cc.)

TABLE XIV

NORMAL POTENTIALS (25°) IN NEUTRAL ALCOHOLIC SOLUTION

System, named as reductant	E_0, v.
p-Aminodiphenylamine	0.751
Hydroquinone	.715
p-Hydroxyphenyl-β-naphthylamine	.701
p-Methyl-*p*′-hydroxydiphenylamine	.684
p,*p*′-Dihydroxy-diphenylamine	.656
2,4-Diamino-4′-hydroxydiphenylamine	.568
β-Phenylhydroxylamine	.562

were prepared from freshly crystallized or distilled material and kept in an atmosphere of nitrogen. In the case of *p*-methyl-*p*′-hydroxydiphenylamine it was necessary to reduce catalytically a small amount of the oxidant which was found to be present.

The potential of the quinone–hydroquinone system was determined by the use of quinhydrone. The potential of such a solution is initially 5–10 mv. above the normal potential. Within one to two minutes it falls to a point where it remains constant for about six minutes, and then it falls off at the rate of about seven mv. per hour. The reading during the period of constancy is reproducible on various electrodes and with different preparations, and this point was taken as the normal potential. On titration of hydroquinone with potassium molybdicyanide, the electrode equilibrium is established slowly and the results are not satisfactory.

β-Phenylhydroxylamine behaved in a very curious manner. The potential of a fresh solution was about 20 mv. higher than the normal potential of the nitrosobenzene–β-phenylhydroxylamine system, whereas one would expect the solution containing none of the oxidant to have a potential considerably below the point of half-oxidation. The initial potential was not constant, but fell off fairly rapidly as the solution was stirred and treated with a steady stream of nitrogen, and in about an hour a fairly constant level had been reached which was 47 mv. below the normal potential. A titration commenced after this or a longer period of time gave perfectly normal results, though electrode equilibrium was somewhat slow. After each addition of molybdicyanide the potential reached a constant value (from below) only after about three minutes. On the other hand, when the titration was commenced ten minutes after preparing the solution, that is, before the low, constant level had been reached, the same amount of oxidizing agent was consumed, but the curve was flat, as though some oxidant were present at the outset, and the value found for E_0 was about 10 mv. too high.

Summary

The unstable systems formed by phenols or amines and the free radicals formed as their immediate oxidation products have been characterized

by a new term called the critical oxidation potential. This is the potential of some oxidizing solution which will cause a certain small amount of the amine or phenol to become oxidized in five minutes when equivalent amounts of the sample and of the oxidizing agent are employed. This value, which may be determined with reasonable accuracy, represents the potential at which the velocity of oxidation becomes vanishingly small, and hence the result is influenced by the reaction rate to an extent which is insignificant. This has been demonstrated experimentally, for the critical oxidation potential bears a definite relationship to the normal potential, and it is influenced no more by temperature changes than is the latter quantity.

The critical oxidation potentials of over seventy compounds have been determined and many relationships, conclusions and deductions have been pointed out in discussing the results.

BRYN MAWR, PENNSYLVANIA

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

SOME ERRORS IN ANALYTICAL BROMINATION. THERMAL CLEAVAGE OF HYDROGEN BROMIDE FROM BROMINATED SUBSTANCES. A NEW PROCEDURE FOR DETERMINATION OF ORGANIC UNSATURATION[1]

BY H. M. BUCKWALTER AND E. C. WAGNER

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I. Introduction

Halogenation methods for the determination of organic unsaturation are in general referable to three types, based upon the nature of the agent and the medium: (1) iodine–halide methods, such as those of Hübl, Wijs and Hanus, conducted in non-aqueous solvents;[2] (2) bromination in non-aqueous solvent, especially carbon tetrachloride, the best-known method being that of Schweitzer–Lungwitz–McIlhiney;[3] (3) the bromide–bromate method, conducted in the presence of water, and due to Koppeschaar.[4]

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[1] Thesis presented by Howard M. Buckwalter to the Graduate School of the University of Pennsylvania in partial satisfaction of the requirements for the degree of Doctor of Philosophy.

[2] Hübl, *Dingler's Polytech. J.*, 253, 281 (1884); *J. Soc. Chem. Ind.*, 3, 641 (1884); Ingle, *ibid.*, 21, 587 (1902); 23, 422 (1904); Wijs, *Ber.*, 31, 750 (1898); Marshall, *J. Soc. Chem. Ind.*, 19, 213 (1900); Kemp, *Ind. Eng. Chem.*, 19, 531 (1927); Hanus, *Z. Nahr. Genussm.*, 4, 913 (1901).

[3] Schweitzer and Lungwitz, *J. Soc. Chem. Ind.*, 14, 130 (1895); McIlhiney, THIS JOURNAL, 16, 275 (1894); 21, 1084 (1899); 24, 1103 (1902).

[4] Koppeschaar, *Z. anal. Chem.*, 15, 233 (1876).

The last method has been applied to determine unsaturation,[5] but is most useful in the analysis of phenols and aromatic amines.[6]

A useful classification of the non-aqueous methods differentiates those which permit determination of only the total halogen consumed and those which attempt its distribution into halogen used in addition and that used in substitution. Methods of the first kind (Hübl, Wijs, Hanus) employ what are probably less severe halogenating agents, especially iodine halides, and short periods of halogenation when possible, with exclusion of light, to minimize substitution. They are satisfactory only when complete addition, without substitution, can be effected under these conditions,' and may not be applicable to compounds whose unsaturation is for any reason less accessible to halogenation.[8] In methods of the second type the extent of substitution is determined by the device of titrating the hydrogen bromide of substitution.[9]

The sample, in an iodine flask, is treated with a measured excess of a standard solution of bromine (or iodine chloride or bromide) in carbon tetrachloride. After a suitable interval (thirty minutes to eighteen hours) potassium iodide solution is introduced, and the liberated iodine, equivalent to the excess halogen, is titrated with thiosulfate. Potassium iodate solution is then introduced, and the liberated iodine, equivalent to the hydrogen bromide of substitution, is titrated. The total halogen consumed. less twice that represented by the second titration, is that taken up by addition.

The only really satisfactory solvent appears to be carbon tetrachloride, in which halogenation is irreversible,[10] and which when properly purified is neutral and not attacked by the dissolved halogen.[11] The greater effectiveness of iodine halide in carbon tetrachloride solution (method of Marshall[2]), compared with that of the solution in acetic acid, was shown by Boeseken and Gelber.[8] Bromine in carbon tetrachloride appears to be equally vigorous. The fact that the increased saturating power of

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[5] Klimont, *Pharm. Post.*, 44, 587 (1911); *Chemical Abstracts,* 6, 1203 (1912); Francis, *Ind. Eng. Chem., 18,821* (1926).

[6] Callin and Henderson, J. *Soc. Chem. Ind.*, 41, 161 (1922); Day and Taggart, *Ind. Eng. Chem., 20,* 545 (1928).

[7] The Wijs method meets these requirements best for the usual fats and oils: "Report of the A. C. S. Committee on Analysis of Fats and Oils," *Ind. Eng. Chem., 18,* 1349, 1354 (1926). To avoid substitution in the analysis of the rubber hydrocarbon, however, Kemp [*ibid.*, 19, 531 (1927)] found it necessary to operate with the Wijs reagent at 0°.

[8] Boeseken and Gelber, *Rec. trav. chim.*, 46, 158 (1927).

[9] Allen, "Commercial Organic Analysis," 2d. ed., Vol. II, p. 383; McIlhiney, and Schweitzer and Lungwitz, Ref. **3.**

[10] In dissociating solvents, including acetic acid, Boeseken and Gelber (Ref. 8) found addition of iodine chloride to be reversible, especially in the neighborhood of negative groups.

[11] Bromine dissolved in chloroform, ethylene bromide or in acetylene tetrabromide generates hydrogen bromide so rapidly that such a reagent cannot be used satisfactorily as a standard solution.

these reagents is accompanied by an increased ability to cause substitution appears to be not a drawback, since the extent of the substitution can be determined.

Both addition and substitution of halogen are influenced, and in ways not always known or predictable, by a variety of factors, including not only time, temperature and quantity and concentration of halogen, but also identity of solvent, condition in which halogen is present, proximity (to the unsaturated condition) of strongly polar radicals or other structural influences, and presence of substances which may operate catalytically. Addition of bromine to unsaturated acids in carbon tetrachloride, according to Williams and James,[12] is catalyzed by traces of hydrogen bromide or water. Davis[13] found light, low temperature and moisture to favor addition of bromine to olefins in carbon tetrachloride. Addition of bromine is retarded by proximity of negative groups,[14] though this influence is not always consistently shown.[15] Difficulty may also be encountered in halogenation of conjugate systems whose saturation is only partial.

Even if it is assumed that addition is initially complete, there are still to be considered several secondary sources of error in methods such as those of Marshall and McIlhiney, due to the reagents added to perform the titrations of the analysis. Several workers[16] have observed replacement of chlorine or bromine by iodine in contact with alkali iodide, in certain cases with subsequent cleavage of iodine to restore the original unsaturation, this effect being favored by negative groups (e. g., —COOH, —$COCH_3$, —COOR, —C_6H_5). Contact of the halogenated sample with water, if followed by hydrolysis, will cause low results by methods in which the HX of substitution is determined.[17] Boeseken and Gelber[S] found that after addition of iodine chloride to certain a,@--unsaturated acids, reversible cleavage of hydrogen chloride became measurable in contact with water, the α-iodo-β-lactone being formed. In the analysis of unsaturated esters, partial ester hydrolysis, promoted by the HX of substitution, would liberate acid which might interfere as indicated below. The presence of water further admits possibility of oxidation by HOX.[18]

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[12] Williams and James, *J. Chem. Soc.,* 343 (1928).

[13] Davis, THIS JOURNAL, 50, 2769 (1928).

[14] Bauer, *Ber.,* 37,3317 (1904); 40, 918 (1907); 44, 2691 (1911); Reich, van Wijck and Waelle, *Helv. Chim. Acta,* 4, 242 (1921); Sudborough and Thomas, *J. Chem. Soc.,* 97,715 (1910).

[15] Biltz, *Ann.,* 296, 231, 263 (1897).

[16] Finkelstein, *Ber.,* 43, 1530 (1910); Biilmann, *Rec. trav. chim.,* 36, 313 (1916); van Duin, *ibid.,* 45,345 (1926); Boeseken and Gelber, Ref. 8; Dillon, Young and Lucas, THIS JOURNAL, 52,956 (1930).

[17] Ingle, *J. Soc. Chem. Ind.,* **21,** 587 (1902); 23,422 (1904); Johansen, *J. Ind. Eng. Chem.,* 14, 288 (1922).

[18] Kolthoff, "Volumetric Analysis," John Wiley and Sons, Inc., New York, 1928, Vol. I, p. 198.

A third source of error is the presence of an acidic function in the substance analyzed. Such acidity would in general be increased by halogenation, and would affect the results to whatever extent the halogenated sample is able to disengage iodine from iodide–iodate solution. Other errors include possible oxidation by iodate, rupture of a chain or bridge followed by additive halogenation of the nascent free ends, and finally the formation of perhalides.[19]

A hitherto unexplained feature of the McIlhiney or Marshall method is that with certain substances the calculated addition values are negative, i. e., the HX found, when multiplied by 2, indicates the halogen consumed in "substitution"[21] to be more than the total halogen brought into reaction. While in some cases negative error is undoubtedly due to incomplete addition, this cannot safely be assumed from the fact that the calculated addition value is low (unless the total consumption of halogen is also low), for the reason that errors due to certain of the secondary interferences mentioned above would also cause low results even when addition was initially strictly quantitative. With existing procedures it is often impossible to determine whether an error is due to unsuccessful halogenation or to secondary reactions during the titrations. Since the latter are caused by contact of the halogenated sample with water, iodide and iodate, it was concluded that a satisfactory study of analytical halogenation could best be made if such contact were avoided. To this end there was developed the aeration procedure for bromination, now to be described.

II. Aeration Method for Determination of Unsaturation by Bromination

Bromination by a solution of bromine in carbon tetrachloride was effected in an evolution apparatus (Fig. *2)* at a suitable temperature, and the excess bromine and the hydrogen bromide produced were removed in a current of dry nitrogen, absorbed in potassium iodide solution, and determined as usual. Except in the case of very volatile substances this procedure avoided contact of the halogenated sample with water, iodide and iodate. In experimental trials of the new procedure, brominations were conducted at 75°, at 20–25° and at 0°. About forty organic substances of various kinds, both unsaturated and saturated, were examined. Comparative analyses were in all cases made by the method of McIlhiney, the bromination period being arbitrarily set at the maximum (eighteen hours).

Apparatus and Reagents

The apparatus consisted of an all-glass evolution flask with a trapped receiver (Fig. *2).* For the aeration, nitrogen from a cylinder was passed through Drechsel bottles charged with (1) alkaline pyrogallol, *(2)* concd. sulfuric acid and (3) granular calcium chloride.

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[19] Kolthoff, Ref. 18, p. 200.

The bromine solution was about 0.28 *N*, containing 7 cc. of bromine per liter of carbon tetrachloride. The best procurable carbon tetrachloride may absorb some bromine and form some hydrogen bromide. It was therefore refluxed for several hours with bromine, cooled, and washed with sodium carbonate solution, dried well over calcium chloride, and distilled through a 5-stage Snyder column, the first and last portions being rejected. It appears that the drying must be thorough, as the presence of moisture was perhaps the cause of subsequent formation of hydrogen bromide in some solutions.

The bromine solution was measured with a 25-cc. Lowy automatic pipet, filled by pressure as suggested in Fig. 1 to avoid the inconvenience and the small loss of bromine involved in filling the pipet by suction.

To standardize the bromine solution, 25 cc. was pipetted into 150 cc. of 15% potassium iodide solution in a 500-cc. iodine flask, and the iodine was titrated with 0.2 *N* thiosulfate, 5 cc. of 0.5% soluble starch indicator being added near the end-point. There was added 10 cc. of 2% potassium iodate solution, and any iodine liberated was titrated. The liquid was shaken vigorously in the stoppered flask near the end of each titration to extract iodine completely from the carbon tetrachloride layer. The second (acid) titration was generally small and sometimes zero.

The 0.2 N sodium thiosulfate was prepared in the usual way, and was standardized against potassium iodate.[20]

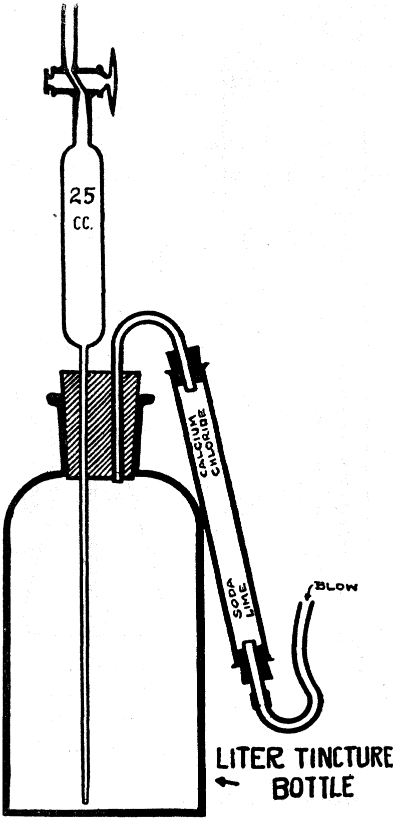

Fig. 1.

Procedure.—Receiver A was charged with 100 cc. of 15% potassium iodide solution, and trap B with 10 cc. of the same, together with about 0.5 cc. of the standard thiosulfate solution, the last being accurately measured from a buret (and its volume finally added to the titration of excess bromine). The sample, in a small glass cup if non-volatile, or in a thin glass bulb or from a Lunge weighing-pipet if a volatile liquid, was introduced into the bromination flask C, and dissolved in 5 cc. of pure carbon tetrachloride. The apparatus was assembled and 25 cc. of the bromine solution introduced by means of the automatic pipet, the tip of which was thrust well into the constriction of D. A gentle suction applied at the trap quickly drew the solution into the flask without loss of bromine. A slow stream of nitrogen (about 20 bubbles per minute) was passed during the ensuing bromination period, at the end of which the flow of gas was increased to about 150–200 bubbles per minute in order to transfer excess bromine, and hydrogen bromide of reaction, as rapidly as possible into the receiver. Repeated blank trials had shown that this operation involved no loss of bromine. The time required for aeration at room temperature was about three and one-half hours.

For bromination at 75° the flask C was immersed, almost to the level of the liquid

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[20] McNabb and Wagner, *Ind. Eng. Chem., Anal. Ed.*, **1**, 32 (1929).

within, in a water-bath at that temperature. During the aeration, which at 75° required only about thirty minutes, carbon tetrachloride was added at intervals to replace that which distilled.

For bromination at 0° the flask C was surrounded by ice, the bromine solution introduced and chilled (with the apparatus assembled), and the sample, in a cup or bulb, introduced into D and washed into the flask with chilled carbon tetrachloride (the bulb being first broken with a glass rod). The aeration at 0° required about six hours.

When the aeration was complete, the apparatus was disconnected at E, the contents of the trap transferred to the main receiver, and the excess bromine and the hydrogen bromide of reaction determined as in the standardization. To calculate, the acid titration, less that of the standardization, was multiplied by 2 and subtracted from the volume of thiosulfate equivalent to the total bromine brought into reaction.

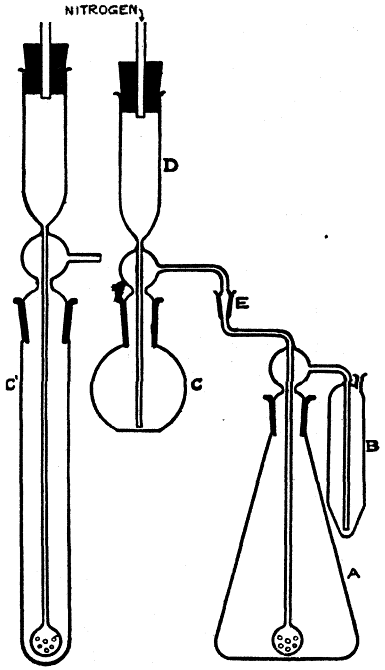

Fig. 2.—A, Receiver, 500-cc. cap.; B, trap, 25-cc. cap.; C, bromination flask, 100-cc. cap.; C′, modified form of C; D, funnel; E, ground joint.

Comparative Results by the Aeration Procedure and by McIlhiney's Method.—Results of comparative trials by the two procedures are grouped below according to the general types of compounds examined, or according to the point to be tested. The tables give total atoms of bromine consumed, atoms of bromine used in "substitution,"[21] atoms of bromine added, and percentage of bromine added, *i. e.*, the bromine number. Check analyses by McIlhiney's method represent duplicates run not in the same series but on different days.

1. Determination of Unsaturation of Some Hydrocarbons.—Results for a number of unsaturated hydrocarbons of several types are given in Table I.

Comments.—A distinct temperature effect is shown for cyclohexene, phenanthrene, indene and especially for retene. The case of pinene, for which both methods yielded values converging upon three atoms of bromine added, recalls similar results obtained by Ingle[1] and by Klimont,[4] and also by Wallach.[22] The facts appear to suggest rupture of the isopropyl bridge.

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[21] As this word is used here and elsewhere in this paper when enclosed in quotation marks, it refers to the apparent substitution indicated by analysis. This is calculated from the hydrogen bromide liberated, whatever its source. When the hydrogen bromide found is believed to include that actually due to substitution and some due also te secondary cleavage of hydrogen bromide during the bromination, the process will be termed "substitution."

[22] Wallach, *Ann.*, 264, 3 (1891).

TABLE I

UNSATURATED HYDROCARBONS

Compound	Method,[a]	Temp., °C	Time, hrs.[b]	Atoms of bromine Total	Subst.	Added	% Br added	Br no. theory
Octylene	A	60	$\frac{3}{4} + 1$	2.27	0.15	1.98	140.9	142.5
B. p. 123.3°		20	$1 + 4$	2.13	.07	1.98	141.2	
	B	Lab.	18	2.72	.42	1.87	133.5	
		Lab.	18	2.65	.36	1.93	137.2	
Cyclohexene	A	75	$1 + \frac{1}{2}$	2.12	.17	1.77	172.7	194.7
B. p. 82.0°		75	$2 + \frac{1}{2}$	1.99	.11	1.77	172.7	
		20	$\frac{1}{2} + 5$	2.04	.07	1.90	185.2	
		0	$1 + 8$	1.99	.03	1.93	187.6	
	B	Lab.	18	2.15	.19	1.78	173.3	
		Lab.	18	2.08	.12	1.85	180.1	
Limonene	A	75	$1 + \frac{1}{2}$	5.55	.72	4.10	240.4	234.7
B. p. 176.6°		75	$1 + \frac{1}{2}$	4.88	.39	4.11	241.0	
	B	Lab.	18	4.60	.31	3.98	233.6	
		Lab.	18	4.68	.35	3.97	233.1	
Styrene	A	75	$4 + \frac{1}{2}$	2.04	.00	2.04	157.0	153.5
B. p. 146.0°	B	Lab.	18	1.96	.02	1.92	147.4	
		Lab.	18	2.07	.02	2.03	155.9	
Stilbene	A	75	$1 + \frac{1}{2}$	2.01	.00	2.01	89.2	88.7
M. p. 124.0°		75	$1 + \frac{1}{2}$	2.00	.00	2.00	88.7	
		75	$1 + \frac{1}{2}$	2.00	.00	2.00	88.7	
	B	Lab	18	2.02	.02	2.00	88.7	
		Lab	18			2.02	89.7	
						2.00	88.7	
Phenanthrene	A	20	$\frac{1}{2} + 6$	2.55	.44	1.68	75.2	89.7
M. p. 99.7°		0	$3 + 7$	2.88	.43	2.02	90.8	
	B	Lab.	18	3.31	.79	1.73	77.6	
		Lab.	18	2.79	.47	1.85	82.9	
Retene	A	75	$1 + \frac{1}{2}$	7.14	3.73	−0.34	−11.8	68.2
M. p. 97.5°		0	$3 + 7$	5.75	1.89	1.97	+67.0	
	B	Lab	18	6.25	2.23	1.79	61.1	
		Lab	18	8.00	3.19	1.62	55.3	
Indene	A	75	$1 + \frac{1}{2}$	4.13	1.21	1.69	116.5	137.7
B. p. 182.8°		25	$0 + 5$	2.17	0.17	1.82	125.1	
		0	$2 + 5$	2.26	.22	1.81	124.4	
		0	$\frac{1}{2} + 7$	2.32	.21	1.89	129.9	
	B	Lab	18	3.91	1.07	1.76	121.3	
		Lab	18	4.29	1.26	1.75	120.6	
Pinene	A	75	$1.5 + \frac{1}{2}$	4.85	1.09	2.67	156.5	117.4
B. p. 158.8°		25	$13 + 3$	4.65	0.89	2.86	167.6	
		0	$\frac{1}{2} + 7$	4.46	.65	3.16	185.4	
	B	Lab.	18	4.55	.83	2.88	169.3	
		Lab.	18	4.80	.91	2.98	174.9	
		Lab.	18	4.29	.63	3.00	176.3	

[a] A, Aeration method, B, McIlhiney's method

[b] First figure indicates time of bromination and second figure time of aeration.

Table II records results obtained with several technical hydrocarbon mixtures obtained from petroleum.[23]

TABLE II

PETROLEUM PRODUCTS

For convenience in comparison, the bromine values obtained are all reported as equivalent iodine values.

Sample	Method	Temp., °C.	Time, hrs.	Equiv. % iodine Total	Subst.	Added	Refinery lab. results Method of Johansen[18] % I Subst.	% I added
Lubricating oil, heavy	A	75	$1 + {}^1/_2$	67.8	38.3	−8.2	10.9	−1.5
		75	$2 + {}^1/_2$	55.1	19.1	−5.5		
		23	1 + 3	33.6	16.4	+0.9		
		0	1 + 7	27.2	12.5	+2.2		
	B	Lab.	18	63.8	35.3	−6.8		
		Lab.	18	44.2	23.2	−1.7		
		Lab.	18	45.4	23.5	−1.8		
Transformer oil	A	75	$1 + {}^1/_2$	62.5	34.6	−6.8	8.3	−0.05
		25	1 + 3	21.0	10.5	−0.1		
		0	1 + 7	15.0	7.1	+0.9		
	B	Lab.	18	64.8	35.1	−5.1		
		Lab.	18	60.0	32.2	−4.4		
Cracked gasoline	A[a]	60	$1 + {}^1/_2$	118.2	43.4	31.3	23.5	32.8
		20	1 + 8	84.8	25.1	34.7		
		0	1 + 6	67.3	14.7	37.8		
	B	Lab.	18	144.8	53.2	38.4		
		Lab.	18	154.0	58.4	37.3		

[a] Sample passed into receiver on aeration.

2. Determination of Unsaturation of Some Compounds with Acidic Character.—Since an iodide–iodate solution is sensitive to acids generally, the effect of an acidic function in the substance analyzed, as was mentioned in the introduction, is to increase the acid titration (after addition of iodate), and to decrease the addition value by double this error. In some cases such acidic function will register quantitatively its acidity, for which deduction can be made in the calculation. If the acidity, however, is of a low order it will introduce an indeterminate error, such irregularity being sometimes suggested by an unusually marked impermanence of the second end-point. Since the causes for error in the bromination of acidic substances are, in general, operative only in the presence of water, etc., such substances are well adapted to test the predictable advantages of the aeration procedure over that of McIlhiney. Results for some unsaturated compounds with acidic function are listed in Table III.

Comments.—The resistance of crotonic acid to halogenation is shown by the ineffectiveness of bromination at room temperature. In McIlhiney's

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[23] Analyzed specimens kindly furnished by the Atlantic Refining Company of Philadelphia, through Dr. J. B. Hill and Mr. E. H. Johansen.

TABLE III

COMPOUNDS WITH ACIDIC FUNCTION

Compound	Method	Temp., °C.	Time, hrs.	Atoms of bromine Total	Subst.	Added	% Br added	Br no., theory
Crotonic acid	A	75	1 + 1/2	2.06	0.05	1.96	182.3	185.7
M. p. 71.8°		75	1 + 1/2	2.07	.03	2.01	187.0	
		20	16 + 3	0.31	.00	0.31	22.6	
	B	Lab.	18	.49	.0	.49	45.6	
		Lab.	18	.58	.0	.58	54.2	
Undecylenic acid	A	60	1 + 1/2	2.04	.12	1.80	78.1	86.8
M. p. 21–22'		22	1 $ 2	1.99	.09	1.80	78.2	
		0	1 + 7	1.89	.05	1.79	77.5	
	B	Lab.	18	2.23	.28	1.67	72.4	
		Lab.	18	2.13	.19	1.75	76.1	
Oleic acid,	A	20	1 + 4	1 99	.11	1.79	50.5	56.6
commercial		0	1 + 8	1.89	.05	1.79	50.7	
	B	Lab.	18	2.19	.24	1.70	48.2	
		Lab.	18	2 19	.23	1.73	48.8	
Fumaric acid	A	75	1 + 2	nil				
	B	Lab.	18	nil				
Maleic acid	A	75	1 + 2	nil				
	B	Lab.	18	nil				
Erucic acid	A	70	1 + 1/2	2.56	.51	1.54	36.3	47.2
M. p. 31–32°		70	0 + 1	2.45	.38	1.70	40.1	
		20	15 + 3	2.50	.40	2.10	49.6	
	B	Lab.	18	3.03	.70	1.64	38.7	
		Lab.	18	2.37	.33	1.72	40.6	
Cinnamic acid	A	75	1 + 1/2	2.02	.00	2.02	109.1	107.9
M. p. 133°		75	1 + 1/2	2.02	.00	2.02	109.2	
	B	Lab.	18	2 00	1.09	−0.19	− 9.9	
		Lab.	18	1.99	0.97	+ .05	+ 2.5	
Abietic acid	A	75	2 + 1/2	10.1	6.70	−3.34	−88.1	52.9[a]
M. p. 155°		75	1 + 1/2	10.37	6.03	−1.69	−44.8	
From Florida		75	0 + 1/2	7.34	3.81	−0.30	− 7.8	
winter rosin		0	0 + 7	4 98	1.65	1.68	+44.3	
		0	1.5 + 8	6.06	1 87	2.33	+61.6	
		0	1 + 7	6 96	2.48	1.99	+52.5	
	B	Lab.	18	10.87	6.56	−2.24	−59.4	
		Lab.	18	9.72	5.37	−1.02	−27.1	
				%	%		%	
Rosin (Florida)	A	75	1 + 1/2	265.4	154.9		−44.4	Nil[b]
		20	1 + 4	187.9	84.8		+18.3	
		0	1 + 7	155.0	61.8		+31.4	
	B	Lab.	18	292.7	173.3		−53.8	
		Lab.	18	285.7	163.8		−41.9	

[a] For 1 double bond and molecular weight 302. [b] According to McIlhiney.[2]

method the sample indicated its acidity quantitatively in contact with aqueous iodide–iodate, the titration due to this effect being deducted to obtain the stated substitution value zero. With cinnamic acid the total consumption of bromine in the McIlhiney method was the theoretical, and results would be excellent if the acid titration were ignored. In contact with water, iodide and iodate, however, the dibromide appeared not only to exert its effect as an acid, but also to suffer extensive hydrolytic breakdown.[24]

In the examination of abietic acid the negative and erratic results obtained by McIlhiney's method, and the rapid and persistent return of color after the acid titration seemed at first to be clear indications of interference by water, etc. The inadequacy of this explanation is shown by the fact that the aeration method at higher temperatures and in absence of water yielded negative values just as large. The improvement between 75 and 0° is relatively enormous, and the largest positive value obtained may still be a partial one, a temperature of 0° being possibly too high for normal bromination. The results indicate roughly one double bond, which duplicates the findings of certain other workers.[25] The behavior of rosin, as would be expected, is similar to that of abietic acid.

3. Bromination of Some Other Compounds.—Results for several other compounds of types not yet considered are given in Table IV. **Ex**amination of cumene, cymene and menthane was undertaken to study the behavior of the isopropyl group, since it seemed possible that bromination of its tertiary carbon might yield a condition susceptible to removal of bromine by hydrolysis, or to cleavage of hydrogen bromide.

TABLE IV

BROMINATION OF SOME ISOPROPYL HYDROCARBONS AND OF SOME ESTERS

Compound	Method	Temp., °C.	Time, hrs.	Atoms of bromine Total	Subst.	Added	% Br added	Br no. theory
Menthane	A	75	1 + ½	447	2.41	−0.35	−19.9	0.0
B. p. 169.0"		30	..	3.56	1.88	−0.21	−12.0	
		25	16 + 4	1.94	0.10	− .04	− 2.3	
		0	2 + 6	0.05	.02	+ .02	+ 0.1	
	B	Lab	18	.23	.08	.06	3.2	
		Lab.	18	.09	.00	.09	5.3	
Cumene	A	75	1 + ½	4.37	2.18	.01	0.5	0.0
B. p. 153.3"		20	1 + 4	5.82	2.86	.08	5.1	
	B	Lab.	18	3.99	1.94	.09	5.9	
		Lab.	18	4.02	1.88	.05	3.6	
Cymene	A	75	1 + ½	6.35	3.14	.06	3.6	0.0
B. p. 153.3"		0	1 + 5	4.77	2.36	.05	2.9	
	B	Lab.	18	4.77	2.74	− .73	−43.4	
		Lab.	18	3.80	2.18	− .58	−34.5	

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[24] Beilstein, 4th ed., Vol. IX, p. 518.

[25] Virtanen *[Ann.,* 424, 163 (1921)] by a semi-quantitative method, and Shaefer *[Ind. Eng. Chem., Anal. Ed., 2,* 115 (1930)], by quantitative hydrogenation in the presence of palladium, both obtained results for one double bond.

TABLE IV (*Concluded*)

Compound	Method	Temp., °C.	Time hrs.	Atoms of bromine Total	Subst.	Added	% Br added	Br no. theory
Ethyl fumarate (Eastman)	A	75	$1 + {}^1/_2$	1 98	0 01	1 96	90 9	92 9
		20	${}^1/_2 + 5$	2.03	.00	2 03	94.3	
	B	Lab.	18	1.02	.0	1.02	47.3	
		Lab.	18	1 33	0	1 33	61.5	
Ethyl maleate (Eastman)	A	75	$1 + {}^1/_2$	1.89	.17	1.55	72.0	92.9
		20	${}^1/_2 + 5$	0.65	.01	0.63	29.5	
	B	Lab.	18	1 80	.09	1.61	74.9	
		Lab.	18	1.45	04	1.38	64.0	
Ethyl oleate (Eastman)	A	75	$1 + {}^1/_2$	2.78	.26	2.26	58.3	51.5
		25	0 + 5	2 63	.10	2.46	62.4	
	B	Lab.	18	3.19	.45	2.30	59.2	
		Lab.	18	3 02	.39	2.24	57.6	

Comments.—The addition of bromine to menthane, cumene and cymene was in all cases slight, the titrations being small (0.18 and 0.31 cc. for menthane). The negative values for cymene by McIlhiney's method were probably due to hydrolytic action. No connection between structure and behavior upon bromination is obvious in the rather unsatisfactory results obtained for these hydrocarbons.

III. The Cleavage of Hydrogen Bromide from Brominated Compounds

The bromine values obtained by the aeration procedure were for certain substances remarkably affected by temperature, the indicated addition decreasing with higher temperatures and even becoming negative in several cases. Lower temperature appeared to favor normal bromination, and was effective in producing normal values with some substances whose bromine numbers at room temperature or at 75° were useless. The total consumption of bromine (addition plus "substitution"), on the other hand, was much increased by higher temperature. Briefly stated, *at higher temperature (e. g., 75°), when the indicated addition was at a minimum or was even negative, the total amount of bromine consumed was at a maximum.* This is illustrated by the following data taken from previous tables.

It seems unlikely that under conditions of maximum consumption of bromine an olefinic condition could escape initial saturation, but even if this were admitted it would provide no explanation for negative addition values obtained in the absence of water. A negative value can here mean only one thing: *hydrogen bromide is being produced in excess of that properly considered as hydrogen bromide of substitution.* Since the aeration procedure excluded contact of the sample with water, iodide and iodate, the production of hydrogen bromide due to hydrolysis or to other causes mentioned in the introduction can be dismissed from consideration. There remains the conclusion that hydrogen bromide may have split out

TABLE V

RELATIONSHIP BETWEEN EXTENT OF "SUBSTITUTION" AND INDICATED ADDITION VALUE

Compound	Temp., °C.	Indicated addition, % Br	Indicated "substitution," % Br
Retene	75	−11.8	255.2
	0	+67.0	129.0
Abietic acid	75	−88.1	354.0
	0	+52.5	131.6
Rosin	75	−44.4	154.9
	0	+31.4	61.8
Heavy lubricating oil	75	− 5.2	23.9
	0	+ 1.4	7.8
Transformer oil	75	− 4.3	21.6
	0	+ 0.5	4.5
Menthane	75	−19.9	274.5
	0	+ 0.1	0.2

spontaneously from a heavily brominated molecule due to instability at the existing temperature. To test this conclusion, samples of several substances were brominated at lower temperatures, freed from bromine and hydrogen bromide in the usual way, and were then heated for thirty to forty-five minutes in the aeration apparatus, any volatile products of this operation being collected in potassium iodide solution in the receiver. The solution in the receiver was treated with starch indicator (no color, showing no free bromine retained in the sample or split out on heating), iodate solution was added, and any liberated iodine was titrated. Excepting menthane, the substances so tested, exhaustively brominated at 0°, yielded hydrogen bromide when heated to 75°, and several lost hydrogen bromide on warming only to room temperature. The hydrogen bromide obtained in these experiments was not merely a qualitative trace, but in several cases approximated in amount the excess hydrogen bromide indicated by the abnormal results of analysis at the higher temperature, though no attempt was made to complete the elimination of hydrogen bromide.

The hydrogen bromide split out of two specimens of abietic acid brominated at low temperature and heated to 75°, if multiplied by two as in the analysis, and subtracted from the addition values at 0°, changes these to —59.8 and —38.6%. Similarly the "corrected values for rosin become —24 and —1.2. The addition value for retene is in the same way reduced from 67 to 23, and that for phenanthrene from 90.8 to 60.8. It is, therefore, shown that the abnormal addition values obtained by bromination at too high temperature may be approached artificially by brominating at low temperature and then splitting out hydrogen bromide by heat.

The cleavage of HX from halogenated organic molecules is, of course, not a new idea,[26] but its possible interference with analytic brominations appears to have been overlooked, That the accumulation of negative atoms or radicals inclines molecules to instability and to cleavage is well known.[27] Cleavage of hydrogen bromide during analysis involves dehydrogenation (oxidation) of the molecule by bromine. The separation of some carbon when paraffins are chlorinated, and especially when methane and chlorine are exploded (with formation of hydrogen chloride in both cases), and many condensations by oxidation, are similar dehydrogenations. So also are such reactions as the formation of hydrogen iodide by heating rosin and iodine,[28] and of hydrogen sulfide by heating paraffin and sulfur.

The simplest result of hydrogen bromide cleavage would be the introduction of a double bond, and under conditions suitable for the saturation of double bonds. A more intimate knowledge of such reactions may show that double bonds are thus introduced in positions inaccessible to subsequent bromination, due to proximity of negative radicals, including bromine atoms firmly held,[29] or to a structural condition such as conjugation. Whatever the explanation, the fact of hydrogen bromide cleavage appears to be established, and its importance in analytic bromination is obvious.

IV. Conclusion

Tables I–IV show that in all but a few cases the aeration method, under suitable temperature conditions, yielded better results than did McIlhiney's method. It is to be noted that by proper temperature control of the brominations negative results were completely eliminated.[30]

The aeration procedure has yielded an explanation for the low or negative bromine values obtained for certain substances, since by exclusion of other sources of error it has brought into prominence the spontaneous cleavage of hydrogen bromide (other than that properly attributable to substitution) from such substances when exhaustively brominated at a

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[26] Kharasch and Darkis [*Chem.* Rev., 5, 601 (1928)] cite the thermal cleavage of hydrogen bromide from triphenylethylene dibromide; and the ready loss of HX from the 9,10-anthracene dihalides is familiar.

[27] See e. g., Henrich (Johnson–Hahn), "Theories of Organic Chemistry," John Wiley and Sons, Inc., New York, 1922, p. 581.

[28] Kastle and Bullock, Am. *Chem. J.*, 18,105 (1896).

[29] *Cf.* Cohen, "Organic Chemistry," Arnold and Co., London, 1928, Vol. I, pp. 125–128.

[30] The accuracy of McIlhiney's method in difficult cases might be improved by operating at 0°, but some error would persist with compounds which before or after bromination are reactive with aqueous iodide–iodate. This interference, while often not important, is apparently quite general in analyses by the McIlhiney procedure, as is shown by the return of the starch–iodide color after the end-point of the acid titration. This secondary liberation of iodine was in several cases (controlled by blanks) observed to continue for weeks.

too high temperature. This conclusion was verified by experimental elimination of hydrogen bromide from several substances brominated at low temperature and then warmed to 75°.

The practical application of the findings by the aeration procedure requires the use of bromination temperatures low enough to prevent excessive consumption of bromine by reactions other than addition, and thereby to prevent or minimize spontaneous cleavage of hydrogen bromide in excess of that actually due to substitution. Some substances brominate normally at 75°, others at room temperature, while others yield entirely meaningless results unless brominated near 0°, which for some substances is perhaps still too high a temperature. The new procedure permits the necessary temperature regulation, and appears to be unique in that it permits bromination at elevated temperature and avoids complications due to contact of water, iodide and iodate with the brominated sample. There is now under investigation a new aeration apparatus designed to effect bromination with a minimal excess of bromine, thus decreasing the quantity of bromine to be transferred by aeration and shortening the analysis, especially when low temperatures are used.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY AND OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

PSEUDO BASES. I. CERTAIN N-METHYLPYRAZINIUM SALTS AND THEIR CORRESPONDING BASES

BY JOHN G. ASTON

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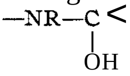
The work of Hantzsch and of Decker[1] has demonstrated that a quaternary base of the type $[-N^{+}R{=}C<]\,OH^{-}$ in which the $N{=}C$ grouping is part of a closed ring (e. g., N-methylpyridinium hydroxide) may exist in two tautomeric modifications. One of these with the formula written above is a quaternary ammonium compound and therefore in aqueous solution necessarily a strong electrolyte.[2] The other weakly basic modification has the formula  $\underset{\displaystyle OH}{-NR-\overset{}{C}<}$ and has been called by Hantzsch a "pseudo base;" it is a tertiary amine and has, to a certain extent, the properties of a carbinol. We shall speak of the equilibrium mixture between these two forms as a "pseudo basic system."

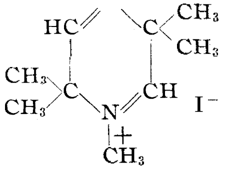
[1] Hantzsch and Kalb, Ber., 32, 3109 (1899); Decker, J. *prakt. Chem.*, 192, 425 (1911).

[2] Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Company, New York, 1923, p. 111.

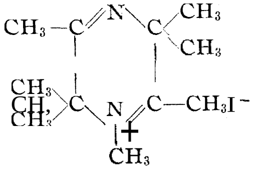
Although certain evidence regarding the properties of and the equilibrium between the two forms has been obtained in the case of some N-methylated pyridines, quinolines and acridines and of cotarnine and berberine,[1] wider information upon a variety of simpler compounds is necessary in order to make any generalizations regarding the effect of structure on the properties of a pseudo basic system.

In order to study the effect of ring conjugation in such a system it was decided to prepare and investigate certain pyrazine derivatives in which a pseudo basic system formed part of the pyrazine nucleus and to study the effect of reduced conjugation caused by partial hydrogenation of the nucleus.

Two salts, 1,2,2,5,5-pentamethyldihydropyrazinium iodide (Formula I) and 1,2,2,3,5,5,6-heptamethyldihydropyrazinium iodide (Formula II) were prepared by the action of methyl iodide on the corresponding dihydropyrazines.



I



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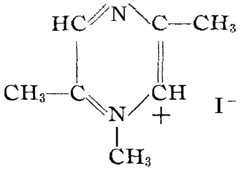

III

In addition, 1,2,5-trimethylpyrazinium iodide (Formula III), already described by Stoehr,[3] was prepared and studied. Bases were prepared from these salts by the action-of potassium hydroxide.

A quarternary salt of the general type $\left[R{-}N{=}C{-}CH_2R\right]^+X^-$ in which the dotted line represents the rest of a cyclic system, might yield the true base, A, $\left[R{-}N{=}C{-}CH_2R\right]^+OH$ or the pseudo base, B, $R{-}N{-}C(OH)CH_2R$. The pseudo base might lose water to form C, $R{-}N{-}C{=}CH{-}R$, or D, $\left[R{-}N{-}C(CH_2R){-}\right]_2O$. In addition the pseudo base may split at the N—C linkage to form E, $RNH\quad COCH_2R$. The form C can also be formed directly from the true base A by a type of change discussed later. A base of the general formula D was obtained by Hantzsch and Kalb[1] as an anhydride of N-methylquinolinium hydroxide. Anhydro bases of the form C are discussed by Decker.[4] The salt I cannot yield a base of the type C. With this exception all five types of base might be yielded by any of the salts.

By the addition of potassium hydroxide to 1,2,2,5,5-pentamethyldihydropyrazinium iodide a base, 1,2,2,5,5-pentamethyl-6-hydroxypyrazine,

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[3] Stoehr, *J. prakt. Chem*., **47**, 463, 470 (1893).

[4] Decker, *Ber.*, 38, 2493 (1905).

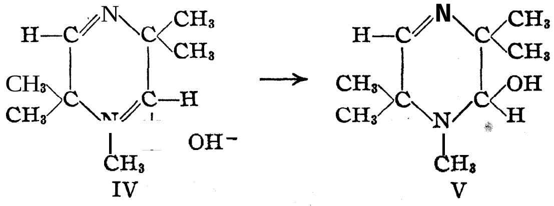
m. p. 110° (Formula V), was isolated. The base is of type B. It is associated in benzene but shows normal molecular weights in water. The normal molecular weight in water shows that the ring system is in all probability stable to water over at least short periods.

By the method of Kohler, Stone and Fuson[5] it was shown that the base reacted with slightly more than two molecules of methylmagnesium iodide per molecule and liberated one molecule of methane, which further points to the presence of the hydroxyl group.

It does not seem likely, in view of these results, that the base to which Formula V has been assigned has undergone ring fission to yield a base of type E, especially as in the open chain the remaining —C=N— would probably be hydrolyzed. Further, no carbonyl derivatives could be obtained from solutions of the base.

Measurement of the conductivity of a dilute solution of equimolar quantities of the iodide and sodium hydroxide by the method of Stewart and Maeser[6] for detecting association of hydroxyl ion showed that there was no strong base present even at 0° immediately after mixing, the base formed having $K_b < 3 \times 10^{-5}$.

In the pseudo basic system from salt I the equilibrium between IV and V is evidently established quite rapidly and is in the direction of the pseudo base, V.



When the base, V, was titrated in water solution with hydrochloric acid, using methyl orange as indicator, at first the neutralization was instantaneous and the indicator stayed yellow until one equivalent of acid per mole had been added. More acid then caused the indicator to turn red but upon standing the yellow color slowly returned. Further increments of acid caused the same effect and finally when two equivalents of acid had been added per mole the red color became permanent.

An explanation of this effect is that the base strength of the pseudo basic system involved in the equilibrium between IV and V is much less than that of the unmethylated nitrogen which is consequently titrated first. Upon adding a fraction of the second equivalent of acid the methylated nitrogen in the strongly basic form (IV) reacts, the methylated nitrogen in the pseudo basic form (V) being so weak that it reacts but slightly

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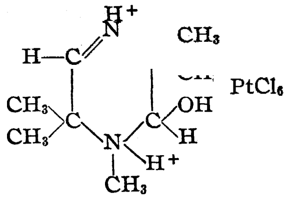
[5] Kohler, Stone and Fuson, This Journal, 49, 3181 (1927).

[6] Stewart and Maeser, *ibid.*, 46, 2583 (1924).

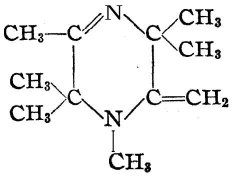
before the methyl orange changes to red. The system being now no longer in equilibrium, more pseudo base changes into the strong base, which reacts with the added acid and the system becomes basic, causing the reappearance of the yellow color.

As would be expected, the original iodide from which the base was prepared, when dissolved in water, produces a system in all ways similar to that produced by adding one equivalent of acid to the base, Addition of hydrochloric acid to the former produced the same changes as those produced by further increments of hydrochloric acid to the latter.

If the iodide of Formula I is changed into the chloride and treated with chloroplatinic acid, a chloroplatinate is obtained whose analysis corresponds to the Formula VI. The same platinum double salt is obtained from the base itself. The possibility that this salt is a hydrated form of the salt of the base IV is unlikely since it is obtained in better yields from solutions of the base in which V predominates.



VI

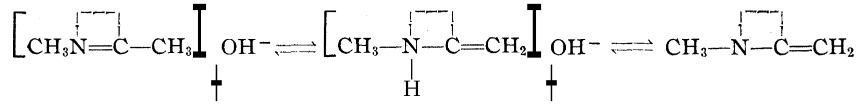


VII

By the addition of concentrated potassium hydroxide to a solution of heptamethyldihydropyrazinium iodide a liquid anhydro base of the type C (Formula VII) was obtained. It showed a normal molecular weight in benzene. This base dissolved slowly in water, yielding a strongly basic solution whose electrolytic conductivity corresponded to a base with a basic dissociation constant of $K_B = 4 \times 10^{-3}$, and was the same as that obtained for an equivalent mixture of original salt and sodium hydroxide after subtracting the conductivity due to the sodium iodide.

The second basic nitrogen in heptamethyldihydropyrazinium iodide was too weak to be titrated using methyl orange as indicator. When the base was titrated rapidly with 0.1 *N* hydrochloric acid using methyl orange as indicator, only one equivalent of acid reacted per mole, the second equivalent of base being too weak to react under these circumstances. Upon allowing a solution of the base, which had a slight excess of acid over one equivalent, to stand, none of the excess acid was used up even on standing. Solutions of the base in water to which no acid had been added underwent slow decomposition and upon titration, after standing, part of the second equivalent of basic nitrogen could be titrated to methyl orange. This pointed to cleavage of the ring in alkaline solution.

It seems necessary in this case to attribute the strong basicity to the methylated nitrogen, which can exist in the quaternary form because the unmethylated nitrogen is formally tertiary and has no possibility of becoming a quaternary base (except by the addition of hydrogen ion). A simple tertiary amine has not been found with $K_B > 10^{-3}$. It is reasonable to assume that the base (Formula VII) is formed from the quaternary base by the following mechanism



$$\left[CH_3N{=}C{-}CH_3\right]^{+} OH^- \rightleftharpoons \left[CH_3{-}\underset{H}{\underset{|}{N}}{-}C{=}CH_2\right]^{+} OH^- \rightleftharpoons CH_3{-}N{-}C{=}CH_2$$

If the pseudo base $\left(CH_3{-}N{-}COHCH_3\right)$ were an intermediate in the production of VII, this would mean that the system is in equilibrium with the pseudo base. Equilibrium with the pseudo base was attained in the basic system from 1,2,2,5,5-pentamethyldihydropyrazinium iodide and an extremely feeble basicity of the methylated nitrogen resulted. If the pseudo bases were in equilibrium with the system under discussion, a weak basicity would also be expected. However, the basic properties of the methylated nitrogen are, in this case, far from weak and therefore equilibrium with the pseudo base or any reaction involving it is thought unlikely. Equilibrium with the quaternary base is probably responsible for the strongly basic properties of VII.

Addition of chloroplatinic acid to concentrated aqueous solutions of the base yielded a chloroplatinate whose analysis corresponded to the chloroplatinate of a base of type B. This same platinum double salt was obtained when a concentrated heptamethyldihydropyrazinium chloride solution which had stood for several days was treated with chloroplatinic acid. It is probable, however, that these chloroplatinates are hydrated forms of salts of bases of type A, especially in view of the large yields (66%) in which it is obtained from the salt.

The above results show that when ring conjugation is absent the mere substitution of a simple methyl group on the carbon atom attached to nitrogen in the system $\left[CH_3\overset{|}{N}{=}\overset{|}{C}{-}\right]^{+} OH^-$ can give rise to a relatively stable anhydro base of type C.

Attempts to obtain a solid or liquid base from 1,2,5-trimethylpyrazinium iodide (Formula III) in a pure state have failed. However, certain evidence has been obtained that in water solution the base, immediately after liberation from the salt, is of the type A in rapid equilibrium with a very small amount of the pseudo base (type B), which slowly changes into an anhydro base of type D. This evidence will be presented in the second paper of this series, where a more detailed study of the equilibrium in and the mechanism of some of the above reactions, which further substantiates the conclusions reached in this paper, is presented.

Experimental

1,2,2,5,5-Pentamethyldihydropyrazinium Iodide.—Thirty-four and a half grams (0.25 mole) of 1,2,2,5,5-tetramethyldihydropyrazine and 34.0 g. (0.24 mole) of methyl iodide dissolved in 123 cc. of sodium-dried ether were allowed to react for thirteen days at room temperature. At the end of this time about 100 cc of dry ether was added and the mixture stirred. The crystalline salt was washed with dry ether; yield, 54.0 g. (0.193 mole) (80.4% of the theoretical); m. p., with decomp., 204°. The material was recrystallized by dissolving in methyl alcohol (1 7 cc. per g) heating to boiling to dissolve and while hot adding twice the volume of n-butyl alcohol. The salt crystallized on cooling, leaving a red solution. The red color is not due to iodine. The crystals were washed with ether; m. p., with decomp , 194". The lowered melting point on crystallization is peculiar.

Anal. Calcd. for $C_9H_{17}N_2I$: I, 45.3. Found: I, (Volhard), 44.69. Recrystallization did not alter this analysis.

1,2,2,3,5,5,6-Heptamethyldihydropyrazinium Iodide.—A solution of 12.2 g. (0.073 mole) of anhydrous hexamethyldihydropyrazine and 12.2 g. (0.069 mole) of methyl iodide in 40 cc, of sodium-dried ether was sealed up in a bomb tube and heated to 85–110° for three days. At the end of this time 100 cc. of dry ether was added to the contents of the bomb tube. The crystalline salt was filtered off and washed with dry ether; yield, 16.6 g. (0.054 mole) (78% of the theoretical); m. p. 249.5° with decomposition. The salt was recrystallized in substantially the same manner described for pentamethyldihydropyrazinium iodide using the same solvents. The mother liquor from the crystallization was also dark red; m. p. of recrystallized product, 249° with decomp

Anal. Calcd. for $C_{11}H_{21}N_2I$: I, 41.1. Found: I (Volhard), 40.4.

Recrystallization did not change this analysis. Rate of heating did not affect the melting point.

When the preparation of this compound was carried out by allowing the same quantities to stand at room temperature for eighteen days the yield was only 26% of the theoretical. Evidently the two extra methyl groups have a marked effect in slowing down the rate of addition of methyl iodide.

1,2,2,5,5-Pentamethyl-6-hydroxytetrahydropyrazine.—Fifteen grams (0.054 mole) of 1,2,2,5,5-pentamethyldihydropyrazinium iodide was dissolved in 30 cc. of water and 100 cc. of 33% potash was added with vigorous stirring. The oil which first separated crystallized to a crust which was filtered off by suction through a Witt plate without filter paper. The excess potassium hydroxide was removed by pressing on a porous plate. The material was dried over calcium chloride and dissolved in 17 cc. of hot benzene. To the hot filtered solution 5 cc. of ligroin (b. p. 40–60°) was added and the mixture shaken. Upon cooling crystallization took place. Finally, after cooling in the ice box, the crystals were filtered off and washed with petroleum ether; yield, 7.6 g. (0.045 mole) (83% of the theoretical); m. p. 108–110°. Further recrystallization in the same way did not alter this melting point.

Anal. Calcd. for $C_9H_{18}N_2O$: C, 63.50; H, 10.65; N, 16.48. Found: C, 63.78; 63.85; H, 10.75, 10.79; N (Dumas), 16.80. Molecular weight in water (freezing point): H_2O, 20.2 g.; sample, 0.3637, 0.3007; ΔT_F, 0.206, 0.160°. Calcd. for $C_9H_{18}N_2O$: mol. wt.. 170.2. Found: mol. wt.. 163, 170.

In Table I are given the results of molecular weight determinations on this compound in benzene. ΔT_F is the lowering of the pure solvent caused by the given total weight of added compound.

Behavior of **1,2,2,5,5-Tetramethyl-6-hydroxytetrahydropyrazine on Titration with Acid.**—Sample: 0.0993 g. of $C_9H_{18}N_2O$ in 50 cc. of water; indicator, methyl orange.

TABLE I

MOLECULAR WEIGHT DETERMINATIONS

Wt. of benzene, 17.4 g.	I	II	III	IV
Total wt. of added compound, g.	0.0698	0.1563	0.1996	0.3354
ΔT_F, °C.	.123	.221	.272	.334
Molecular weight	167	208	216	286.5

These results show that the compound is quite highly associated in benzene.

The solution was titrated dropwise with vigorous shaking, using 0.1339 *N* hydrochloric acid solution. After 6.3 cc. of acid had been added the indicator turned definitely orange but changed back to yellow in forty-five seconds. Further increments of acid changed the indicator to red but the yellow color returned after about five-minute intervals. After 8.65 cc. of acid had been added the indicator became permanently red. Calcd.: cc. of 0.1339 N HCl required for 1st equivalent. 4.35; 2d equivalent, 8.70.

Addition of excess acid and back titration with alkali to the orange-yellow end-point after allowing to stand for two hours showed that the total acid required by the compound was 8.72 cc. Equivalent weight, calcd., 85.1. Found: 85.0.

Behavior of 1,2,2,5,5-Pentamethyldihydropyrazinium Iodide on Titration with Acid.—A solution of 0.1970 g. of the salt in 50 cc. of water was titrated with 0.1339 N hydrochloric acid as in the above experiment. After 2.80 cc. of acid had been added the methyl orange changed from yellow to red and then, over a distinct time interval, back to yellow. After 3.53 cc. had been added, a 0.74-cc. increment of acid produced a red color which changed back to orange-yellow in about five minutes. This effect continued throughout the titration. After 5.60 cc. had been added the solution became permanently red. Back titration with alkali showed 5.42 cc. of acid to have been used (calculated, 5.25 cc.). Alkali equivalent to all the acid which had been added was introduced and the titration repeated after allowing to stand for seven minutes. After 3.16 cc. of acid had been added, a red color changing back to yellow appeared. The effect continued until all the added alkali had been used up. Unquestionably, the effect is reversible.

The Reaction of **1,2,2,5,5-Tetramethyl-6-hydroxytetrahydropyrazine** with **Methyl** magnesium Iodide.—The apparatus and method used was as described by Kohler, Stone and Fuson[6] with slight modifications.[7] To 0.0995 g. of compound was added 4.31 cc. of a 0.573 *M* solution of methylmagnesium iodide in isoamyl ether; 14.6 cc. of methane (corrected to S. T. P.) was liberated. The excess Grignard reagent upon treatment with water (4.05 cc.) yielded 25.1 cc. of methane (corrected to S. T. P.). Methane per mole of compound, 1.11 moles. Total CH_3MgI used per mole of compound, 2.31.

1,2,2,5,5-Pentamethyl-6-hydroxytetrahydropyrazine Chloroplatinate.—Thirty-four hundredths g. (0.002 mole) of **pentamethyl-6-hydroxytetrahydropyrazine** was dissolved in 5 cc. of water. Excess of 1 N chloroplatinic acid was added. The precipitated chloroplatinate was insoluble in hot alcohol and in hot water and could not be crystallized; yield, 0.74 g. (0.00127 mole) (63% of the theoretical); m. p. (with decomp.) 282°. The temperature of the bath in which this salt decomposed in ten seconds was 320°.

Anal. Calcd. for $C_9H_{20}N_2O{\cdot}PtCl_6$: Pt, 33.66. Found: Pt, 33.88.

By allowing the base to stand with hydrochloric acid for twenty minutes before adding the chloroplatinic acid, the above yield was reduced to 30%.

The same platinum double salt could be obtained from 1,2,2,5,5-tetramethyldi-

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[7] We wish to thank Mr. J. D. Pickens, Research Fellow in Chemistry at The Pennsylvania State College for these results.

hydropyrazinium iodide. A solution of 1.4 g. (0.005 mole) of 'the salt in 10 cc. of distilled water was stirred with 0.01 mole of silver chloride for sixteen hours. The chloroplatinate was precipitated with excess *M* chloroplatinic acid from the filtered solution of the chloride; yield, 0.3 g. (0.00052 mole) (10% of the theoretical); m. p. with decomp. 284–285° (started with bath at 130°). In the bath at 320° it decomposed in ten seconds.

Anal. Calcd. for $C_9H_{20}N_2O \cdot PtCl_6$: Pt, 33.66. Found: Pt, 33.65.

The two salts were unquestionably identical.

1,2,2,3,5,5-Hexamethyl-6-methylenetetrahydropyrazine.—Fourteen grams of heptamethyldihydropyrazinium iodide was dissolved in 35 cc. of water and 62 cc. of 40% potassium hydroxide was added. The non-aqueous layer was separated and dried for two hours over potassium hydroxide sticks and for one hour over anhydrous potassium carbonate. The filtered liquid was distilled *in vacuo* under 6.5 mm. pressure and the distillate collected in two portions: (1) 70 (about)–78.°, 1.1 g.; (2) 78.0–78.2°, 5.4 g. Both fractions were colorless; total yield of both fractions, 6.5 g. (79% of the theoretical). The fraction of b. p. 78.0–78.2° was used for analysis, molecular weight determinations, etc.

Anal. Calcd. for $C_{11}H_{20}N_2$: C, 73.28; H, 11.18. Found: C, 72.75, 73.08; H, 10.76, 10.83. *Molecular weight* by freezing point lowering in benzene: C_6H_6, 17.4 g.; sample, 0.1580, 0.1986 g.; ΔT_F, 0.261, 0.325". Mol. wt. calcd. for $C_{11}H_{20}N_2$: 180.2. Found: 178.2, 179.9.

The base undergoes decomposition slowly at room temperature to yield a red viscous oil.

Titration of 1,2,2,3,5,5-Hexamethyl-6-methylenepyrazine with Hydrochloric Acid.—The base was dissolved in 50 cc. of water and titrated immediately and rapidly to the yellow-orange end-point of methyl orange. Sample: 0.1754 g. required 7.45 cc. of 0.1339 N HCI. Eq. wt.: calcd. for $C_{11}H_{20}N_2$ (as a mono-acid base), 180.2. Found: 175.8. This equivalent weight was checked by adding excess acid and back titrating with alkali. Excess alkali equivalent to 5 cc. of the acid was then added and solution allowed to stand for three and one-half hours at room temperature. Upon back titrating to the yellow-orange end-point, the total acid used up by the base was found to have increased by 2.89 cc., corresponding to about 50% decomposition. In another experiment the base was allowed to stand in 50 cc. of water for about five minutes and then titrated to the orange end-point of methyl orange. Sample: 0.2243 g. required 10.80 cc. of 0.1339 *N* HCl. Eq. wt., found: 155.1, *i. e.*, 1 mole of base yielded 1.161 eqts. of titratable base, corresponding to 16.1% decomposition in five minutes at room temperature. Excess acid was added and the solution after standing for four hours was back titrated. The net amount of acid required by the base was unchanged. This points to the stability of the base in acid.

Upon titration 0.5674 g. of the heptamethyldihydropyrazinium iodide was found to require 0.09 cc. of 0.1339 N hydrochloric acid to reach the orange end-point of methyl orange.

The chloroplatinates from 1,2,2,3,5,5,6-heptamethyldihydropyrazinium iodide and from 1,2,2,3,5,5-hexamethyl-6-methylenetetrahydropyrazine were prepared by methods already described. The salt from the two sources was apparently the same; chloroplatinate from iodide, m. p. about 285° with decornp.; yield, 66%.

Anal. Calcd. for $C_{11}H_{24}N_2O \cdot PtCl_6$: Pt, 32.10. Found: Pt, 31.99.

These chloroplatinates underwent decomposition when crystallization was attempted. The large yield from the salt seems to indicate that the chloroplatinate is a hydrated form of the salt of the quaternary base.

Attempted Isolation of a Base Corresponding to 1,2,5-Trimethylpyrazinium Iodide.—

1,2,5-Trimethylpyrazinium iodide was prepared by the methylation of 2,5-dimethylpyrazine and recrystallized as described by Stoehr.[8] The product melted at 238° with decomposition whereas Stoehr records 230°.

Two grams of the iodide was dissolved in 5 cc. of water and 15 cc. of water and 15 cc. of 33% potassium hydroxide was added. The gum which separated was pressed out on a porous plate and dissolved in pure pyridine. After drying with solid potassium hydroxide for one hour the solution was treated with three times its volume of dry ether. A yellow crystalline material separated. This was filtered off by suction and washed several times with ether. The substance became dark red on standing. Its analysis varied from C, 53.2; H, 6.94, to C, 49.5; H, 6.63 on standing in a dry atmosphere for a day. This analysis does not correspond to that of any of the expected bases. Upon melting it gave a curious behavior. Heated slowly, it blackened at about 88° and melted at 179–190°, but, placed in a bath at 146°, it melted immediately. Evidently decomposition took place on slow heating. This compound will be investigated further. Various other attempts to obtain a pure base failed.

The experimental data upon the base strength of the above bases are recorded in the second paper of this series.

Summary

1. 1,2,2,5,5-Pentamethyldihydropyrazinium iodide and 1,2,2,3,5,5,6-heptamethyldihydropyrazinium iodide have been prepared.

2. 1,2,2,5,5-Pentamethyldihydropyrazinium iodide yields the base 1,2,2,5,5-pentamethyl-6-hydroxytetrahydropyrazine, whereas 1,2,2,3,5,5,6-heptamethyldihydropyrazinium iodide yields 1,2,2,3,5,5-hexamethyl-6-methylenetetrahydropyrazine. The ease of formation of the latter compound is attributed to lack of conjugation.

3. Possible tautomeric systems arising from these bases are discussed and related to their behavior on titration and salt-forming properties.

4. No base corresponding to 1,2,5-trimethylpyrazinium iodide could be isolated.

STATE COLLEGE, PENNSYLVANIA

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[8] Stoehr, *J. prakt. Chem.*, 47,463,470 (1893).

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

STEREOCHEMISTRY OF DIPHENYL COMPOUNDS. THE PREPARATION AND RESOLUTION OF 2-METHYL-6-NITRO-2'-CARBOXYDIPHENYL. XI[1]

BY R. W. STOUGHTON[2] AND ROGER ADAMS

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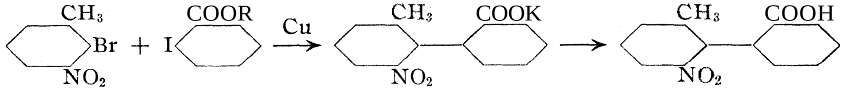
In a recent article[3] the desirability of studying 2,2',6'-trisubstituted diphenyls in connection with the stereochemistry of the diphenyl series was pointed out. In this first communication of several covering such compounds is given the description of the preparation and properties of 2-methyl-6-nitro-2'-carboxydiphenyl (I). This is the first diphenyl prepared which has had merely three groups substituted in the two rings, and in addition it is the first in which each of the 2,2',6'-positions has been filled by different groups.[4]



(I)

The compound was resolved and the two optical antipodes isolated. They racemized only very slowly and the properties were essentially in accord with what had been predicted from the x-ray data.

By boiling in butyl alcohol or in acetic acid, racemization took place partially over a period of thirty to forty hours. On the other hand, on boiling a sodium hydroxide solution of the compound, partial racemization occurred in four hours. Kuhn and Albrecht[6] have found when working with diphenyl derivatives that the decrease in optical activity obeys the law of a first order reaction and have expressed the speed of racemization in terms of the half-life periods. This furnishes at least a semi-quantitative measure of the stability of such compounds under different conditions. Using the same method, the half-life period at 117° in butyl alcohol is forty-two hours; at 118° in acetic acid is thirty-four hours; and at 100° in 0.1 N sodium hydroxide solution, four and one-half hours. This compound was stable to racemization at room temperatures in any of the solvents mentioned above.

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[1] For the last article in this series see Stecle and Adams, THIS JOURNAL, **52, 4528 (1930).**

[2] This communication is in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Steams and Adams, THIS JOURNAL, **52, 2070 (1930).**

[4] During the preparation of this manuscript an article has appeared by Lesslie, and Turner [J. Chem. *Soc*, 1758 (1930)] describing another compound of this latter type 2,4-dinitro-6-carboxy-2'-methyldiphenyl.

[5] Kuhn and Albrecht, Ann, **455, 272 (1927); 458, 221 (1927).**

From x-ray data[6] the distances between the groups can be estimated. Using the values and calculations similar to those given in a previous paper, the interference between the methyl and the carboxyl groups will be \$0.39 Å., between the nitro and the carboxyl groups +0.58 Å.; hence stability to racemization might be expected. The hydrogen and the nitro group or the hydrogen and the carboxyl group will not collide (—0.06 Å. and −0.42 Å., respectively).

In previous papers[2,3] the possibility of the rings bending toward each other when approaching the same plane so as to allow free rotation was discussed and this may account for the gradual racemization observed at high temperatures over a period of time. In sodium hydroxide solution at 100° the rate of racemization was almost ten times as fast as in butyl alcohol at 117°. Since it is known that an ionized carboxyl group is smaller than one which is un-ionized, such a difference in racemization rate is to be expected.

Kuhn has studied the ease of racemization of 2,4′-dinitro-6,6′-dicarboxydiphenyl and 2,4,4′-trinitro-6,6′-di-carboxydiphenyl and found them more easily racemized than the compound just described. This might be expected in the light of the same reasoning previously outlined.

The 2-methyl-6-nitro-2'-carboxydiphenyl was prepared by condensing under carefully specified conditions 3-nitro-2-bromotoluene with methyl o-iodobenzoate by means of copper. The resulting mixture was saponified, which allowed the removal of the alkali-insoluble 2,2′-dinitro-6,6′-dimethyldiphenyl. There was apparently little or no 2,2′-dicarboxydiphenyl found, so that on acidification essentially pure 2-methyl-6-nitro-2'-carboxydiphenyl was obtained. The compound was resolved through the brucine salt. The conversion of this nitro compound to the corresponding amine and thence to the corresponding halogen compounds is now under way so that a direct comparison of several groups on rate of racemization may be obtained.

Experimental

2-Bromo-3-nitrotoluene.—A solution of **38** g. of 3-nitro-o-toluidine (prepared by the method of **Hadfield** and **Kenner**),[7] in **650** cc. of glacial acetic acid, 60 cc. of water and 39 g. of **concd.** sulfuric acid, was cooled in an ice-salt bath and to it a solution of **45** g. of sodium nitrite in **75** cc. of water was added slowly with constant stirring. At the same time a **cuprous** bromide solution was prepared by refluxing a mixture composed of 46 g. of crystallized copper sulfate, **125** g. of sodium bromide, **75** g. of copper turnings, **80** g. of concd. sulfuric acid and **325** cc. of water, until its color was light yellow. After standing for two hours in the cold, the **diazotized** solution was added to the cuprous bromide solution and steam distilled. The distillate was extracted with ether. The product amounted to **37** g. **(68%)**, boiling at **161–164°** at **30 mm**. and melting at **39–40.5°**.[8]

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[6] Stanley and Adams, This Journal, **52,1200 (1930).**

[7] **Hadfield** and Kenner, Proc. Chem. *Soc.*, **30,253 (1914).**

[8] Gibson and Johnson, **J.** Chem. *Soc.*, **1244 (1929)**, give the boiling point as **135.** at 6 mm., **157°** at 22 **mm.**, and the melting point as **41–42'.**

Methyl *o*-Iodobenzoate.—*o*-Iodobenzoic acid was prepared by the method of Wachter[9] and esterified in the following manner. A solution of 62 g. of o-iodobenzoic acid in 500 cc. of absolute alcohol was saturated with dry hydrogen chloride and refluxed for five hours. This solution was then poured into water, neutralized with potassium carbonate and extracted with ether. It was finally distilled under diminished pressure. A yield of 50 g. (78%) boiling between 165–168° at 25 mm. was obtained.

2-Methyl-6-nitro-2'-carboxydiphenyl.—In a 200-cc. 3-necked flask fitted with a mechanical stirrer and reflux condenser, was placed 37 g. of bromonitrotoluene and 38 g. of methyl-o-iodobenzoate. This was heated in a metal-bath and as soon as the contents just began to boil, 50 g. of copper bronze was slowly added. During the addition, which required about three-quarters of an hour, the temperature of the bath was kept between 270 and 280°. When all of the copper had been added, the bath temperature was raised to 300° for fifteen minutes. During the course of the reaction the mixture turned dark brown and considerable heat was evolved. After cooling, it was thoroughly extracted with ether and filtered. The ether was removed by evaporation and the oily residue saponified by refluxing for four hours with 10% sodium hydroxide. A little black tar insoluble in the alkali remained, which proved to be 2,2'-dimethyl-6,6'-dinitrodiphenyl. This was removed by filtration and the filtrate acidified slowly with dilute hydrochloric acid. A brownish-black tar separated which quickly solidified. This crude product was dissolved in 400 cc. of benzene, boiled with norite for ten minutes and filtered. The color of the solution changed at this time from a dark brown to an orange red. After concentrating to 50–60 cc., the benzene solution was extracted twice with 10% sodium hydroxide, and upon acidification with dilute hydrochloric acid, 16 g. of crude yellow product was obtained. No diphenic acid, the third theoretical product of this reaction was isolated. The crude product was recrystallized three times from dilute alcohol. A yield of 12 g. (27%) of pure product was obtained. Pure methyl nitrocarboxydiphenyl is a pale yellow solid melting at 171–172°, soluble in the common organic solvents but insoluble in cold water.

Anal. Calcd. for $C_{14}H_{11}NO_4$: C, 65.35; H, 4.31. Found: C, 65.56; H, 4.44.

Resolution of 2-Methyl-6-nitro-2'-carboxydiphenyl.—To a boiling solution of 2 g. of 2-methyl-6-nitro-2'-carboxydiphenyl in 1500 cc. of water was added 3.07 g. of anhydrous brucine. As soon as solution was complete, it was filtered and at the end of one-half hour 2.1 g. of flaky white crystals had deposited. These were collected and after three recrystallizations from water yielded one gram of salt of constant rotation melting from 169–175°. This salt was found to contain water which corresponds to one molecule of water of crystallization. The analytical sample was dried over phosphorus pentoxide in a vacuum at 117° for twenty-four hours. The melting point of the anhydrous form is 173–175°.

Rotation. Hydrated l-salt: 0.1368 g. made up to 25 cc. with chloroform at 20° gave $\alpha_D = +0.33°$; $l = 2$; $[\alpha]^{20}_D +30.4°$.

Anal. 0.3304 g. lost 0.0086 g. on drying. Calcd. for $C_{37}H_{37}N_3O_8{\cdot}H_2O$: H_2O, 2.69. Found: H_2O, 2.60. Calcd. for $C_{37}H_{37}N_3O_8$: C, 68.17; H, 5.73. Found: C, 67.67; H, 5.75.

Upon concentrating the mother liquors to 100 cc., 1.8 g. of impure d-salt was obtained. This was recrystallized from water and on each crystallization the very first crystals that separated were discarded. Five recrystallizations in this manner yielded 0.5 g. of salt with a constant rotation melting from 145–155°. This salt appears to contain water equivalent to one and one-half molecules of water of crystallization. The anhydrous form which was used for analysis melts at 172° with softening beginning at 145°.

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[9] Wachter, Ber., 26, 1744 (1893).

Rotation. Hydrated d-salt. 0.0850 g. made up to 15 cc. with chloroform at 20° gave $\alpha_D = -0.65'$; 1 = 2; $[\alpha]^{20}_D$ −57.3".

Anal. 0.1780 g. lost 0.0070 g. on drying. Calcd. for $C_{37}H_{37}N_3O_8 \cdot 1.5\ H_2O$; H_2O, 3.98. Found: H_2O, 3.93. Calcd. for $C_{37}H_{37}N_3O_8$: C, 68.17; H, 5.73. Found: C, 67.86; H, 5.93.

l and *d*-**2-Methyl-6-nitro-2′-carboxydiphenyl.**—The active acids were liberated from their salts by treatment with hydrochloric acid in the cold. The organic acid was obtained as a fine cream-colored powder when 0.77 g. of the I-salt (less soluble) was shaken with 6 *N* hydrochloric acid for one hour. This was filtered, washed with dilute hydrochloric acid and finally with water. After two recrystallizations from dilute methyl alcohol, 0.21 g. remained melting at 174–175° with slight softening at 168°.

Rotation. I-acid. 0.2052 g. made up to 25 cc. with methyl alcohol at 20° gave $\alpha_D = -1.11°$; 1 = 2; $[\alpha]^{20}_D$ −67.7'.

The d-acid was obtained in exactly the same way; melting point 171–173° with slight softening at 167°.

Rotation. d-acid. 0.0309 g. made up to 15 cc. with methyl alcohol at 20° gave $\alpha_D = +0.26°$; $l = 2$; $[\alpha]^{20}_D$ +63.1°.

Racemization Experiments

1. A sample of the I-acid was dissolved in ordinary ethyl alcohol and refluxed in a flask with a ground-glass joint for twenty-four hours. No change in rotation was observed.

Rotation. 0.0950 g. made up to 25 cc. with ethyl alcohol at 20° gave $\alpha_D = -0.52°$; $l = 2$; $[\alpha]^{20}_D$ −68.4".

2. **A** second sample of the 1-acid was refluxed in butyl alcohol in the same manner as in ethyl alcohol; 0.0583 g. was made up to 15 cc. at 20°, $l = 2$. $k = l/t \log_{10} \alpha_0/\alpha_t$; half-life period $= l/k \log_{10} 2$.

Time in minutes	α_D	$[\alpha]^{20}_D$	k	Av. k
0	−0.56°	−72.0°	. . . .	
360	− .49°	−63.0"	0.00016	
1080	− .42°	−54.0"	,00012	0.00115
1740	− .35°	−45.0°	.00010	
2460	− .32°	−41.3'	.00010	

Half-life period = 2510 minutes = 42 hrs.

3. **A** sample was then dissolved in glacial acetic acid and treated in the same manner: 0.0840 g. was made up to 15 cc. at 20', 1 = 2.

Time in minutes	α_D		k	Av k
0	−0.97"	−86 6°	. . .	
180	−0 90°	−80 4°	0 00018	
540	−0 82°	−73 2°	00013	0 00015
1080	−0 69°	−61 6°	00014	

Half-life period = 2007 minutes = 34 hrs.

4. The I-acid was dissolved in 5% sodium carbonate and allowed to stand for twenty-four hours at room temperature. The rotation did not change.

Rotation. 0.1148 g. made up to 15 cc. with 5% sodium carbonate solution at 20° gave $\alpha_D = +0.33°$; $l = 2$; $[\alpha]^{20}_D$ +21.6°.

5. A sample of I-acid dissolved in 0.1 N sodium hydroxide solution did not change in rotation upon standing for twenty-four hours at room temperature, nor upon heating for two hours at 80°. The solution was then refluxed but due to the small rotation in sodium hydroxide the rotations were taken on the free acid in methyl alcohol.

Rotation. 0.1140 g. made up to 15 cc. with 0.1 N NaOH at 20° gave $\alpha_D = +0.19°$, $1 = 2$; $[\alpha]_D^{20}$ +12.6°.

Time in minutes	$[\alpha]_D^{20}$ in CH_3OH	k	Av. k
0	−67.7"	....	
120	−50 6°	0.0011	0.00115
300	−29.0"	.0012	

Half-life period = 262 minutes = 4.5 hrs.

Summary

1. The compound 2-methyl-6-nitro-2′-carboxydiphenyl has been prepared and resolved.

2. The active forms racemize slowly in boiling alkali and still more slowly in neutral or acid solvents.

URBANA, ILLINOIS

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

HEXA-OMEGA-TERTIARY-BUTYLPROPINYLETHANE AND SOME NEW ACETYLENIC CARBINOLS

BY I. L. OZANNE AND C. S. MARVEL

RECEIVED OCTOBER 9, 1930 PUBLISHED DECEMBER 18, 1930

In attempting to find some aliphatic unsaturated hydrocarbons which would resemble the hexa-arylethanes, several tetra- and hexa-acetylenic ethanes have been prepared in this Laboratory.[1] All of the compounds which have been described heretofore have had as the acetylenic group the radical *tert.*-butylethinyl, $(CH_3)_3C—C\equiv C—$. In order to learn more about compounds of this general type, the work has now been extended to cover hydrocarbons in which other than tertiary alkyl groups are attached to the ethinyl group. It has been shown[2] that a tertiary alkyl group directly attached to the central carbon of a hexasubstituted ethane has a greater effect in producing dissociation than does a secondary alkyl group, and this in turn has a greater effect than does a primary alkyl group. It has seemed of interest to determine whether this effect is transmitted through the acetylenic structure to the central ethane carbon. As the first step in this study, the preparation and properties of a hexa-

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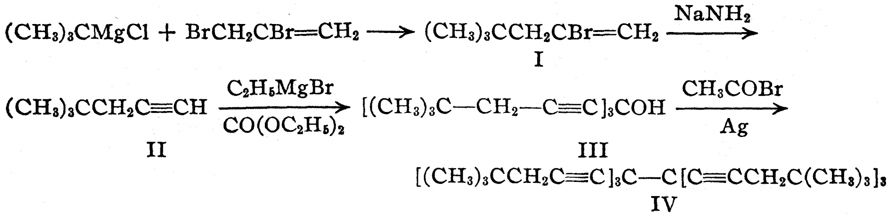
[1] The publications describing these compounds are Salzberg and Marvel, THIS JOURNAL, 50, 1737, 2840 (1928); Rossander and Marvel, *ibid.*, 51,932 (1929); Gillespie and Marvel, *ibid.*, 52, 3368 (1930).

[2] Conant, Small and Sloan, ibid., 48, 1743 (1926); Conant and Bigelow, *ibid.*, 50, 2041 (1930).

acetylenic ethane which has a primary alkyl group attached to the ethinyl group are described in this communication.

The synthesis of hexa-ω-*tert.*-butylpropinylethane was accomplished in the following manner



$$(CH_3)_3CMgCl + BrCH_2CBr{=}CH_2 \longrightarrow \underset{I}{(CH_3)_3CCH_2CBr{=}CH_2} \xrightarrow{NaNH_2}$$

$$\underset{II}{(CH_3)_3CCH_2C{\equiv}CH} \xrightarrow[CO(OC_2H_5)_2]{C_2H_5MgBr} \underset{III}{[(CH_3)_3C{-}CH_2{-}C{\equiv}C]_3COH} \xrightarrow[Ag]{CH_3COBr}$$

$$\underset{IV}{[(CH_3)_3CCH_2C{\equiv}C]_3C{-}C[C{\equiv}CCH_2C(CH_3)_3]_3}$$

The first two compounds in this series, 4,4-dimethyl-2-bromopentene-1 (I) and 4,4-dimethylpentine-1 (II) were prepared according to the general method of Lespieau and Bourguel.[3] The carbinol (III) was prepared by the method described by Salzberg and Marvel[1] for tri-*tert.*-butylethinylcarbinol. It was impossible to convert this carbinol to a crystalline bromide which could be purified. However, the desired hydrocarbon (IV) was obtained by treating the carbinol with acetyl bromide and then with metallic silver. The same product was obtained when these two reactions were carried out in separate operations that was obtained when all of the reagents were mixed together and the synthesis accomplished in one step.

The structure of the new hydrocarbon was not as easily determined as was that of hexa-*tert.*-butylethinylethane. Treatment of hexa-ω-*tert.*-butylpropinylethane with liquid sodium–potassium alloy gave a colored alkali metal derivative that reacted with dry carbon dioxide to give an acidic compound which could not be purified. Oxidation of the hydrocarbon with ozone gave about 30% of the calculated amount of *tert.*-butylacetic acid. These facts are in agreement with the structure which has been proposed for the hydrocarbon.

The hydrocarbon was not cleaved by 1% sodium amalgam and hence is more stable in this respect than hexa-*tert.*-butylethinylethane. It is less stable in air and does not keep well. After it is a few hours old it begins to develop a yellow color and in one day turns brown due to decomposition or polymerization. The nature of the change has not been determined.

Several other intermediate compounds containing primary alkyl groups attached to an acetylenic linkage have been obtained and are described in the experimental part. However, their conversion to hexasubstituted ethanes has not been accomplished. One hydrocarbon has been described as di-ω-*tert.*-butylpropinyl-tetraphenylethane but this structure is only supported by the method of synthesis.

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[3] Lespieau and Bourguel, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1926, Vol. VI, pp. 20, 26.

Experimental Part

4,4-Dimethyl-2-bromopentene-1.—In a three-liter, three-necked flask fitted with a mechanical stirrer, a reflux condenser and a separatory funnel, was placed 200 g. of bromo-allyl bromide and 200 cc. of anhydrous ether. The flask was placed in an ice-bath, and through the separatory funnel was added an ether solution of 1.33 moles of *tert.*-butylmagnesium chloride which had been prepared and titrated previously. The Grignard reagent was added at such a rate that the ether boiled gently. The addition required about thirty to forty-five minutes After the addition was complete, the ice-bath was removed *and* the mixture was gently refluxed on a water-bath for about two hours in order to insure completion of the reaction.

The mixture was then cooled and the excess Grignard reagent was decomposed by adding slowly a solution of 35 cc. of concentrated hydrochloric acid in 350 cc. of water through the separatory funnel. The ether layer was separated, washed with a saturated solution of sodium bicarbonate, dried over calcium chloride and distilled. After the ether was removed, the 4,4-dimethyl-2-bromopentene-1 was collected at 135–138°. The yields varied from 80 to 110 g. (45–62% of the theoretical amount); d_4^{20} 1.030, n_D^{20} 1.4630.

Anal. Subs., 0.1930: 26.26 cc. of 0.04137 N $AgNO_3$. Calcd. for $C_7H_{13}Br$: Br, 45.2. Found: Br, 45.0.

In order to obtain a pure product it was always necessary to use an excess of the Grignard reagent so that no unreacted bromoallyl bromide (b. p. 140") remained in the mixture.

4,4-Dimethylpentine-1.—Sixty-two grams of sodamide was ground in a mortar with 104 cc. of purified high-boiling mineral oil until a fine suspension was obtained. This was transferred to a 1-liter round-bottomed three-necked flask fitted with a reflux condenser protected with a calcium chloride tube, a 500-cc. separatory funnel, and an efficient mechanical stirrer, An additional 125 cc. of mineral oil was used in transferring the suspension from the mortar to the reaction flask. The mixture was heated in an oil-bath at 160–165°, the stirrer was started, and 92 g. of 4,4-dimethyl-2-bromopentene-1 was added from the dropping funnel.

The reaction started at once and ammonia was evolved. Heating and stirring were continued for two hours after the addition of the bromo compound was complete. The mixture was then cooled, diluted with 250 cc. of xylene and this solution was poured onto about 700 g. of cracked ice to which had been added 140 cc. of concentrated hydrochloric acid (sp. gr. 1.19). The oil layer was separated, washed with a saturated solution of sodium bicarbonate, dried over calcium chloride and distilled from a modified Claisen flask.[4] In the first fractionation the material boiling between 50 and 100" was saved. On redistillation the product boiling at 73–75' at ordinary pressures was collected. The yield was 18 g. (37% of the theoretical amount). There was some loss in the preparation due to the heptine passing off with the ammonia. By using ice water in the condenser and washing the ammonia which escaped with the xylene which was used to dilute the reaction mixture, the yield was increased to 45% of the theoretical amount. The new acetylene has the following constants: d_4^{20} 0.7154, n_D^{20} 1.4028.

The acetylene was not analyzed as such, but was converted to the diacetylenic mercury compound $[(CH_3)_3CCH_2C{\equiv}C]_2Hg$ according to the general method recently described by Johnson and McEwen.[5] The mercury derivative melted at 125–126.5° (corr.).

Anal. Subs., 0.1924: Hg, 0.1000. Calcd. for $C_{14}H_{22}Hg$: Hg, 51.28. Found: Hg, 51.9.

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[4] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 40.

[5] Johnson and McEwen, THIS JOURNAL, 48,469 (1926).

Tri-ω-*tert.*-butylpropinylcarbinol.—To 166 cc. of a 3.0 N solution of ethylmagnesium bromide in dry ether was added 48 g. of 4,4-dimethylpentine-1. The ethane generated by the reaction was led out through a well-cooled condenser to avoid loss of the acetylene. When this reaction was complete, 19.7 g. of diethyl carbonate was slowly added. After about fifteen hours the reaction mixture was decomposed with an aqueous ammonium chloride solution which contained a little hydrochloric acid. The ether layer was separated, washed with water and sodium bicarbonate solution and dried over anhydrous sodium sulfate.

The ether was evaporated and the carbinol was distilled under reduced pressure. The product boiled at 140–142° at 0.7 mm. The yield of distilled product was 42 g. The distillate solidified and was recrystallized from petroleum ether. The yield of recrystallized material was 32.3 g. (68% of the theoretical amount) of a product which melted at 50–51°.

Anal. Subs., 0.1853: CO_2, 0.5704; H_2O, 0.1805. Calcd. for $C_{22}H_{34}O$: C, 84.07; H, 10.82. Found: C, 83.95; H, 10.90.

Hexa-ω-*tert.*-butylpropinylethane.—A solution of 1.5 g. of the carbinol and 0.2 cc. of acetyl bromide in about 10 cc. of dry petroleum ether was allowed to stand for about ten minutes. The petroleum ether and excess acetyl bromide were then removed by evaporating under reduced pressure. A few drops of methyl alcohol were added to decompose any excess acetyl bromide and the mixture was evaporated again under reduced pressure. The residue was taken up in dry ether, 0.5 g. of molecular silver added and the mixture shaken overnight. After filtering, the solvent was evaporated and the residue was recrystallized from a mixture of methyl alcohol and ether. There were thus obtained crystals which melted at 127.5–128.5°.

The same hydrocarbon was obtained more readily by shaking a solution of carbinol and acetyl bromide in petroleum ether with molecular silver. To an ice-cold solution of 1.66 g. of carbinol in 20 cc. of petroleum ether was added 1.7 g. of molecular silver and 0.5 cc. of acetyl bromide. The flask was swept out with dry nitrogen and sealed. The mixture was shaken for eighteen hours. It was then filtered and the solvent evaporated. The residue on recrystallization yielded 0.4 g. (24% of the theoretical amount) of a product of m. p. 127.5–128.5°. A mixed melting point showed this product to be identical with the one obtained above.

Anal. Subs., 0.1986: CO_2, 0.6455; H_2O, 0.1985. Calcd. for $C_{44}H_{66}$: C, 88.88; H, 11.11. Found: C, 88.65; H, 11.08.

This hydrocarbon turns yellow on standing in the air for a few hours. In one day the color deepens to brown. If kept at 0° it remains colorless for over a week. A dry ether solution of the ethane reacted almost instantly with liquid sodium–potassum alloy to give a red metal alkyl. The ethane did not react with 1% sodium amalgam. The result with 40% sodium amalgam was inconclusive. It was not possible to convert the metal alkyl to a crystalline acid by the action of dry carbon dioxide followed by mineral acid. Evidence was obtained repeatedly that an acidic compound was produced but it seemed very unstable and turned to a brown tarry product.

***Tert.*-butylacetic Acid.**—A solution of 30 g. of 4,4-dimethyl-2-bromopentene-1 in 200 cc. of carbon tetrachloride was placed in a wash bottle which was packed with an ice–salt mixture. Ozonized air was passed through the solution at the rate of seven liters per minute for about twelve hours. Additional carbon tetrachloride was added occasionally to replace that swept out by the current of air. Some solid ozonide separated from solution. Dilute aqueous alkali was added and the mixture was heated. The carbon tetrachloride layer was separated and evaporated and the residue was again heated with aqueous alkali. The alkaline solutions were combined and acidified with sulfuric acid and the aqueous solution was distilled until no more oil came over. The distillate was extracted with ether and the ether was removed by evaporation. The residue was distilled under ordinary pressure. There was thus obtained 7 g. of acid which boiled at 186–188° and gave a neutral equivalent of 118.3 instead of the theoretical 116. The p-bromophenacyl ester was formed by refluxing an alcohol solution of the sodium salt with *p*-bromophenacyl bromide. After crystallizing repeatedly this product melted at 81–81.5°.

Anal. Subs., 0.3786: 29.56 cc. of 0.04137 *N* $AgNO_3$ Calcd. for $C_{13}H_{17}O_3Br$: Br, 25.56. Found: Br, 25.82.

Ozonization of **Hexa-*ω*-*tert.*-butylpropinylethane.**—An ice-cold solution of 2.94 g. of the ethane in 200 cc. of carbon tetrachloride was treated with a current of ozonized air at the rate of about 4 liters per minute for about two hours. The ozonized mixture was treated with a little water and then sodium hydroxide solution was added. The carbon tetrachloride solution was thoroughly extracted with the aqueous alkali. The alkaline solution was separated, acidified with sulfuric acid and distilled. An oily acid came over. This distillate was titrated with standard alkali and assuming that all of the acidity was due to *tert.*-butylacetic acid the yield was 0.965 g. (28% of the theoretical amount). The neutral solution was evaporated to dryness, the residue was taken up in 35 cc. of 95% alcohol and 2.03 g. of p-bromophenacyl bromide was added. After boiling to complete the reaction, the derivative was isolated and crystallized. It melted at 80.5–81.5° and was shown by a mixed melting point determination to be identical with the derivative prepared before from *tert.*-butylacetic acid.

ω-*Tert.*-butylpropinyl-diphenylcarbinol.—To 19 cc. of 3.7 *N* ethylmagnesium bromide solution was added 7 g. of 4.4-dimethylpentine-1. The mixture was allowed to stand until no more ethane was evolved and then 7.9 g. of benzophenone was added. The mixture was stirred for about five hours and allowed to stand overnight. On working up the reaction mixture in the usual manner, the carbinol was obtained as a liquid boiling at about 135° under 0.4 mm. pressure. It crystallized readily from petroleum ether and then melted at 55–56°. The yield was 10.3 g. (85% of the theoretical amount).

Anal. Subs., 0.2184: CO_2, 0.6886; H_2O, 0.1556. Calcd. for $C_{20}H_{22}O$: C, 86.33; H, 7.91. Found: C, 85.98; H, 7.96.

ω-*Tert.*-butylpropinyl-diphenyl-bromomethane.—A solution of 0.5 g. of the carbinol in 10 cc. of petroleum ether was treated with 0.2 cc. of phosphorus tribromide. After about one-half hour the solution was washed with sodium bicarbonate solution, dried over sodium sulfate and evaporated under reduced pressure. The residue was a light brown liquid which would not crystallize even when cooled in solid carbon dioxide. This liquid was dried in a vacuum desiccator over phosphorus pentoxide and analyzed.

Anal. (Stepanow) Subs., 0.2040: 6.15 cc. of 0.1000 N $AgNO_3$. Calcd. for $C_{20}H_{21}Br$: Br, 23.53. Found: Br, 24.11.

***Sym.*-di-*ω*-*tert.*-butylpropinyl-tetraphenylethane.**—The crude bromide prepared from 2 g. of carbinol and 0.74 g. of phosphorus tribromide in petroleum ether was treated with 1.5 g. of molecular silver and the mixture was shaken for about twelve hours. The mixture was then filtered, the solvent was evaporated and the residue was crystallized from alcohol. There was thus obtained 0.2 g. of a hydrocarbon which melted at 116–118°. Analysis showed that it had the expected composition. It gave a red color when treated in dry ether with liquid sodium–potassium alloy. However, the metal alkyl thus obtained could not be converted into the corresponding acid.

Anal. Subs., 0.1791: CO_2, 0.6000; H_2O, 0.1305. Calcd. for $C_{40}H_{42}$: C, 91.97; H, 8.03. Found: C, 91.38; H, 8.13.

Di-*ω*-*tert.*-butylpropinyl-phenylcarbinol.—This carbinol was prepared in the same general manner described before. From 18 cc. of 3.6 *N* ethylmagnesium bromide solu-

tion, 6.5 g. of **4,4-dimethylpentine-1** and 5.2 g. of ethyl benzoate there was obtained 3.8 g. of a product boiling at 135–137' at 0.4 mm. pressure: d_4^{20} 0.9325; n_D^{20} 1.5080.

Anal. Subs., 0.2139: CO_2, 0.5979; H_2O, 0.1391. Calcd. for $C_{21}H_{28}O$: C, 85.14; H, 9.46. Found: C, 84.60; H, 9.59.

Diphenyl-ω-cyclohexylpropinylcarbinol.—From 21.6 cc. of 3.8 N ethylmagnesium bromide solution, 10.5 g. of cyclohexylpropine and 14.5 g. of benzophenone there was obtained 6 g. of product which boiled at 210–215° at 1.1 to 1.3 mm. pressure; d_4^{20} 1.058; n_D^{20} 1.5750. This product was redistilled at 0.003 mm. pressure and then boiled at 165–166°.

Anal. Subs., 0.2043: CO_2, 0.6505; H_2O, 0.1459. Calcd. for $C_{22}H_{24}O$: C, 86.84; H, 7.89. Found: C, 86.85; H, 7.99.

Phenyl-di-ω-cyclohexylpropinylcarbinol.—From 35 cc. of 4.2 N ethylmagnesium bromide solution, 18.5 g. of cyclohexylpropine and 11.4 g. of ethyl benzoate there was obtained 4 g. of this carbinol; b. p. 180–185° at 0.017 mm. pressure; d_4^{20} 1.014; n_D^{20} 1.5390.

Anal. Subs., 0.1986: CO_2, 0.6258; H_2O, 0.1635. Calcd. for $C_{25}H_{32}O$: C, 86.20; H, 9.19. Found: C, 85.94; H, 9.21.

Summary

1. Hexa-ω-*tert.*-butylpropinylethane has been prepared and has been found to be less readily cleaved by alkali metals than hexa-*tert.*-butylethinylethane. However, it decomposes with greater rapidity in the air.

2. Some new acetylenic carbinols having primary alkyl groups next to the acetylenic linkage have been described.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OR YALE UNIVERSITY]

PHOTOCHEMICAL OXIDATION OF LACTIC ACID[1]

BY G. RICHARD BURNS

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The present study is a development and a continuation of an investigation of the action of ultraviolet radiation on lactic acid. In the absence of oxygen it has been shown that the main products of the decomposition are ethanol and carbon dioxide.[2] It was felt that the conflicting results obtained by other investigators[3] of this decomposition were due to the presence of oxygen dissolved in the solution.

The decomposition of lactic acid in the presence of oxygen has never been fully investigated. Some workers[4] in this field have exposed solutions of lactic acid to sunlight and air and have obtained qualitative tests

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[1] A part of a paper presented at the Cincinnati meeting of the American Chemical Society.

[2] Bums, THIS JOURNAL, 51, 3165 (1929).

[3] See Neuberg, *Biochem.* Z., 39,163 (1912); Baudisch, *ibid.*, **103**, 59 (1920).

[4] See Ganassini, *Chem.* Zentr., I, 387 (1913); I, 729 (1910); Chemical Abstracts, 5, 3236 (1911); Ciamician and Silber, *Ber.*, 46, 1558 (1913).

for acetic acid, pyruvic acid, acetaldehyde and carbon dioxide. Others[5] have exposed solutions of lactic acid containing uranyl sulfate and measured the amount of uranyl sulfate reduced and the amount of acetaldehyde formed.

In the present investigation a solution of lactic acid was shaken with oxygen while being exposed to the visible and ultraviolet radiation from a quartz mercury lamp. Radiation of wave length longer than 2890 Å. was only slightly absorbed. Thermochemical data[6] show that the decomposition of a dilute solution of lactic acid into dilute ethanol and a saturated solution of carbon dioxide evolves about 3.7 kilogram calories. The longest wave length of radiation that accomplishes this change is equivalent to 112 kilogram calories. It is not surprising that the ethanol formed under these conditions reacts with oxygen dissolved in the solution. The main products of the reaction are acetaldehyde, a peroxide and acetic acid. Quantitative data were obtained on all the above products, as well as on the other substances formed in smaller amounts. Ethanol and pyruvic acid were not found in the reaction mixture. The amount of oxygen used was determined.

Apparatus.—The apparatus was substantially the same as that previously described.[2] A Hullet gas buret[7] was introduced between the reaction vessel and the Topler pump by means of a three-way stopcock in order to measure the amount of oxygen introduced. This buret and the gas analysis buret were in a water-bath kept at 25.0° by a thermostat. The shields between the mercury arc and the reaction vessel were removed so that the latter received the same amount of radiation over the full length of its stroke.

Experimental Part

Before all experiments, the quartz windows were cleaned with cleaning solution, the thermostat filled with distilled water, and the temperature brought to 25.0°. The reaction tube contained 21.38 cc. of 1.140 *N* lactic acid, enough to make it about half full. The rate of shaking was 310 r. p. m. with a 6-cm. stroke. With a total pressure of oxygen and water vapor of 760 mm., the solution dissolved 0.70 cc. (2.8×10^{-5} mole) of oxygen. The usual procedure was to evacuate the system, after the reaction vessel containing the solution had been attached, then to introduce a measured quantity of oxygen, start the shaking and illuminate the solution for one hour. During this time the pressure was held at 760 mm. and the decrease in the gas volume observed. Inasmuch as from 5 to 17 cc. of carbon dioxide remained dissolved in the solution, the decrease in volume was large. At the end of an hour the gas was about 50% oyxgen. The gas was then pumped into the gas analysis buret, the reaction vessel being shaken to remove the carbon dioxide in solution, and analyzed for carbon dioxide, decrease in volume on ignition, and carbon dioxide produced by ignition. The oxygen used was

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[5] See Neuberg, *Biochem.* Z., 13, 305 (1908); 29, 279 (1910); Bolin, Z. *physik. Chem.*, 87,490 (1914); Miiller, *Biochem.* Z., 178, 77 (1926).

[6] Meyerhoff, *ibid.*, 129, 594 (1922); "International Critical Tables," Vol. V.

[7] Taylor and R. M. Burns, THIS JOURNAL, 43,1275 (1921).

assumed to be the volume introduced minus the volume recovered. The volume recovered was taken to be the volume of the gases after the removal of the carbon dioxide minus the volume of carbon dioxide produced on ignition. The aldehyde produced had no effect on the gas analysis in the one-hour runs. In the following tables all gas volumes are corrected to the dry gas at 0° and 760 mm. All distillations and analyses were carried out in all-glass apparatus.

Dark Reaction Rate.—As far as could be observed there was no reaction in the dark.

Oxygen–Carbon Dioxide Ratio.—On illumination, the volume of the gas in the system was found to decrease with a slowly diminishing rate for about eighty-five minutes, followed by a sudden evolution of about 4 cc. of gas. For this reason the runs were limited to sixty minutes. Numbers 1 and 2 in Table I are the results of two runs which were continued for five hours with the gas in the system analyzed and fresh oxygen introduced each hour. Run 3 was made with 50% lactic acid. Tables II and IV include one-hour runs.

TABLE I

VALUES IN CC.

	1st hour	2d hour	3d hour	4th hour	5th hour
			Run 1		
Oxygen absorbed	**16.7**	**21.9**	**23.7**	**26.0**	**27.4**
Carbon dioxide produced	**13.62**	**19.87**	**23.07**	**26.01**	**28.08**
Decrease on ignition	**0.13**	**0.13**	**0.27**	**0.28**	**0.30**
Carbon dioxide by ignition	.20	**.20**	.25	**.25**	**.31**
			Run 2		
Oxygen absorbed	**16.6**	**21.0**	**23.0**	**24.4**	**25.8**
Carbon dioxide produced	**13.16**	**19.43**	**22.04**	**24.00**	**25.07**
Decrease on ignition	**0.08**	**0.13**	**0.22**	**0.22**	**0.26**
Carbon dioxide by ignition	.16	**.16**	**.19**	**.21**	**.27**
		Run 3			
Oxygen absorbed	**38.5**	**34.2**	**35.2**		
Carbon dioxide produced	**27.17**	**29.53**	**33.47**		
Decrease on ignition	**0.18**	**0.27**	**0.28**		
Carbon dioxide by ignition	**.36**	**.62**	**.34**		

Carbon Dioxide–Acetic Acid Ratio.—After the aldehyde and the alcohol had been removed from the reaction mixture by distillation through a fractionating column, the residue and washings of the column were made up to 100 cc. and distilled. Water was admitted as fast as it distilled out and the process continued until 300 to 500 cc. of distillate had collected. Preliminary experiments showed that the greater part of the acetic acid distilled with the first 250 cc. This distillate was divided into two equal portions, one titrated with barium hydroxide to find the total acidity, the other oxidized by the Bourcart–Kuriloff[8] method to determine the lactic acid which had also distilled. Under these conditions this amounted

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[8] Poznanski, THIS JOURNAL, **50,981 (1928).**

to about one-third of the total acid distilling. Table II gives the results of one-hour runs. In order to be sure that the rate of shaking was not a limiting factor, Experiments **3** and 4 of Table II were carried out with half the usual quantity of lactic acid and with the shaking rate increased from **310** to ***375*** r. p. m. In five one-hour runs on the same sample of lactic acid, the yield of acetic based on carbon dioxide was 70.3%.

TABLE II

VALUES IN MOLES X 10^{-6}

Run number	1	2	3	4
Oxygen absorbed	888	819	670	585
Carbon dioxide produced	719	674	577	520
Decrease on ignition	3.5	4		
Carbon dioxide by ignition	6.3	7.6		
Acetic acid formed	536	507	452	400
Yield of acetic on carbon dioxide. %	74.5	75.2	78.4	77.0

Acetaldehyde–Acetic Acid Ratio.—No gas analyses were made in these experiments because of the danger of removing some of the aldehyde. The aldehyde and the alcohol were removed by distillation through a 15-cm. glass bead rectifying column and the residue analyzed in the usual manner. Half the aldehyde–alcohol mixture was analyzed by oxidation, half was analyzed for alcohol after the aldehyde had been removed by distillation from sodium bisulfite and the sulfurous acid removed by distillation from basic solution. At the same time two samples of lactic acid were similarly analyzed for alcohol. No correction was made for the amount of formaldehyde in the acetaldehyde. Colorimetric determinations indicated that a series of five one-hour runs produced over five times the amount of acetaldehyde that was produced in one hour.

TABLE III

VALUES IN MOLES X 10^{6}

Acetaldehyde	236	228
Ethanol	14	13
Ethanol in lactic acid	14	14
Acetic acid formed	597	612
Acetaldehyde oxidized to acetic acid, %	71.7	72 8

Peroxide Formation.—As soon as the period of illumination was over the contents of the tube were run into an acid solution of potassium iodide. At the end of an hour the liberated iodine was titrated. I and II were one-hour runs, III was a five-hour run with fresh oxygen supplied every hour.

I	5.12 cc. of 0.098 N $Na_2S_2O_3$ or 0 000251 moles of peroxide
II	5.40 cc. of .100 *N* $Na_2S_2O_3$ or 000270 moles of peroxide
III	4.56 cc. of .123 N $Na_2S_2O_3$ or .000280 moles of peroxide

When the reaction mixture was allowed to stand for forty-eight hours before analysis the peroxide content dropped to 0.00010 mole and the aldehyde to 0.00012 mole.

Formaldehyde.—The aldehyde fraction of the distillate from the reaction mixture turned Schiff's reagent blue in the presence of sulfuric acid. Formaldehyde gives this reaction while acetaldehyde does not. The approximate amount of formaldehyde present was determined by a colorimetric method based on this reaction. To one-quarter (5 cc.) of the distillate were added **5** cc. of **1** to **3** sulfuric acid and **5** cc. of basic fuchsin almost decolorized by sulfurous acid. The color developed was compared with that developed by 5 cc. of standard formaldehyde solution treated in the same manner. The concentration of the standard solution was determined by oxidation.

One-quarter of distillate was 1.24 stronger than the standard
One-quarter of distillate was 1.23 stronger than the standard
80 cc. standard = 0.56 cc. of 0.200 N $K_2Cr_2O_7$ or 0.000009 mole
10 cc. standard = 0.066 cc. of 0.200 N $K_2Cr_2O_7$ or 0.000008 mole

The residue from the distillation gave a test with Schiff's reagent. The substance giving this test was not identified.

Formic Acid.—No satisfactory test for formic acid in the presence of lactic and acetic acid was found. Formic acid reduces silver nitrate in acid solution while none of the known constituents of the reaction mixture does. The reaction mixture reduces silver nitrate, producing less silver than that reduced by 0.000004 mole of formic acid in a mixture containing lactic acid, formaldehyde and acetaldehyde in the same proportions as the reaction mixture. The residue of the reaction mixture which was left after steam distillation of the acetic acid did not reduce silver nitrate, while the distillate did so.

Quantum Yield.—The quantum yield in the decomposition reaction is probably between 0.5 and 1.0. Absorption measurements on the oxidation reaction mixture show that, after one hour of illumination, it absorbs about **35%** more radiation than the lactic acid. These measurements were made with two thermopiles and galvanometers so that the amount of radiation from the lamp and the amount transmitted by the solution could be determined simultaneously. Several pairs of determinations were made in which the solution was exposed without oxygen for one hour, then oxygen was admitted and the solution exposed for another hour. An attempt was made to keep the radiation constant for each pair of runs. The results are given in Table IV.

Wave Lengths Absorbed.—The following absorption measurements were made in the reaction tube as soon as it was removed from the thermostat. Unoxidized lactic acid absorbed completely to 2535° Å. After one hour of oxidation it absorbed to 2894° Å., after **five** hours some of the

TABLE IV

VALUES IN CC.

	No O_2	O_2	No O_2	O_2	No O_2	O_2
	I		II		111	
Oxygen	..	16.3	..	14.7	..	15.4
Carbon dioxide	4.07	13.57	3.78	12.63	3.77	13.62
Decrease on ignition	0.54	0.18	0 52	0.11	0.40	0.13
Carbon dioxide by ignition	.63	.15	.63	.18	.48	.20
Times increase of carbon dioxide		3.33		3.34		3.61
Times increase in moles of gases		3.02		3.03		3.34

line at 2967 Å. The 50% lactic acid absorbed some of the 2700 Å. line at the start. The alkaline solution of sodium lactate absorbed some of the 3300 Å. line after four hours of oxidation.

Oxidation of the Lactate Ion.—A solution was prepared which contained two equivalents of sodium hydroxide to one of lactic acid, the lactic acid being in the same concentration as in the previous runs. The quantities of oxygen used per hour in a four-hour run were: 3.81, 3.12, 3.29, 2.96 cc.

Subsequent Dark Reactions.—After the gases had been removed the reaction mixture was allowed to stand in the dark for twenty-four hours, the gas formed during this time was removed, and the process repeated at the end of the next twenty-four hours.

TABLE V

VALUES IN CC.

	Run 1		Run 2	
	24 hours	48 hours	24 hours	48 hours
Carbon dioxide	2.36	0.65	1.86	0.66
Ignition	0.36	.06	0.38	.19
Carbon dioxide on ignition	.18	.03	.18	.10

Pyruvic Acid.—No pyruvic acid was found in the reaction mixture although the test used would have shown the presence of 5 X 10^{-5} mole.

Discussion of Results

On the basis of the amount of carbon dioxide evolved: the oxygen used was 118%; peroxide formed, 32%; pyruvic acid, none; carbon monoxide, 0.4%. As the oxidation was continued for longer periods, the carbon dioxide given off became equal to the oxygen used. The amount of peroxide in the solution remained constant after the first hour of oxidation. The aldehyde concentration increased. The above results are the only ones that represent the condition of the reaction mixture at the end of the period of irradiation. In the distillation which is necessary for the analysis of the other products, the peroxide may decompose or may react with certain constituents of the reaction mixture. The products isolated by distillation were acetic acid, 75% (on carbon dioxide);

acetaldehyde, 28%; formaldehyde, 1%; ethanol, none; formic acid, not more than 0.4%. When the solution was allowed to stand for forty-eight hours before analysis, an additional 12% of carbon dioxide was evolved, the peroxide content dropped to 10% and the aldehyde to 12%. The quantum yield in this reaction is several times that of the decomposition reaction without oxygen. The above figures are unavoidably subject to certain errors inasmuch as the amount of lactic acid decomposed was extremely small and the separation of the decomposition products from the undecomposed acid and from each other was difficult.

The results do not exclude the possibility that one of the reactions follows this course: the lactic acid is first decomposed into carbon dioxide and ethanol. The ethanol, which must contain part of the energy from the absorbed radiation, is then oxidized to acetaldehyde. This acetaldehyde is oxidized to acetyl peroxide, probably after the absorption of additional radiation. Bowen[9] has recently shown this to be the case with acetaldehyde and oxygen alone. The acetyl peroxide subsequently reacts with acetaldehyde to give acetic acid. In order to account for the amount of oxygen used it would be necessary to assume the formation of some compound other than those described. No such compound could be identified although the reaction mixture contained a non-volatile reducing agent. Work is now being undertaken on propionic acid in the hope that this point will be cleared up. A similar decomposition of pyruvic acid shows that the reaction proceeds iii a manner which is entirely unlike that of lactic acid.

Summary

1. When lactic acid is decomposed by ultraviolet radiation in a solution containing dissolved oxygen, the chief products are carbon dioxide, acetaldehyde, a peroxide and acetic acid. The amount of each of these decomposition products has been measured.

2. Neither ethanol nor pyruvic acid is formed.

NEW HAVEN, CONNECTICUT

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[9] Bowen and Tietz, *J. Chem. Soc.*, 132,234 (1930).

[COMMUNICATION NO. 46 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & CO.]

STUDIES ON POLYMERIZATION AND RING FORMATION. VII. NORMAL PARAFFIN HYDROCARBONS OF HIGH MOLECULAR WEIGHT PREPARED BY THE ACTION OF SODIUM ON DECAMETHYLENE BROMIDE

BY WALLACE H. CAROTHERS, JULIAN W. HILL, JAMBS E. KIRBY AND RALPH A. JACOBSON

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No rationally synthetic and practical methods for the preparation of giant individuals of the simpler homologous series are available, and one of the objects of the experiments here reported was to explore the possibilities of bifunctional Wurtz reactions as a means of access to this realm.

The first step in simple Wurtz reactions is the formation of the corresponding sodium alkyl, RNa.[1] This normally couples with the halide, forming the hydrocarbon R-R, but it may react in other ways and yield by-products. Sodium ethide reacts with diethyl ether

$$C_2H_5Na + (C_2H_5)_2O = C_2H_6 + C_2H_5ONa + C_2H_4{}^{2}$$

and one may expect the formation of considerable amounts of the hydrocarbon RH when the Wurtz reaction is carried out in that solvent,

The experiments presently described are concerned with the action of sodium on decamethylene bromide in ethereal solution, and the normal course of this reaction including that due to the participation of the solvent (but ignoring for the moment the possibility of intramolecular reaction) may be formulated as follows

$$\begin{aligned}
&Br(CH_2)_{10}Br + 2Na = Br(CH_2)_{10}Na + NaBr\\
&Br(CH_2)_{10}Na + (C_2H_5)_2O = H(CH_2)_{10}Br + C_2H_5ONa + C_2H_4\\
&Br(CH_2)_{10}Na + Br(CH_2)_{10}Br = Br(CH_2)_{20}Br + NaBr\\
&H(CH_2)_{10}Br + 2Na = H(CH_2)_{10}Na + NaBr\\
&H(CH_2)_{10}Na + (C_2H_5)_2O = H(CH_2)_{10}H + C_2H_5ONa + C_2H_4\\
&H(CH_2)_{10}Na + H(CH_2)_{10}Br = H(CH_2)_{20}H + NaBr\\
&H(CH_2)_{10}Na + Br(CH_2)_{10}Br = H(CH_2)_{20}Br + NaBr\\
&H(CH_2)_{10}Na + H(CH_2)_{20}Br = H(CH_2)_{30}H + NaBr\\
&H(CH_2)_{10}Na + Br(CH_2)_{20}Br = H(CH_2)_{30}Br + NaBr\\
&H(CH_2)_{30}Br + 2Na = H(CH_2)_{30}Na + NaBr\\
&H(CH_2)_{30}Na + Br(CH_2)_{20}Br = H(CH_2)_{50}Br + NaBr, \text{ etc.}
\end{aligned}$$

The product will be composed of individuals–of the general formula $H[(CH_2)_{10}]_xH$ and possibly of similar chains terminated at one or both ends by bromine atoms. The length of these chains will be determined by the relative rates of reaction of the sodium compounds with the solvent and with the halides. Solubility effects may also come into play.

The suitability of this reaction as a source of straight chain hydrocarbons will depend upon the extent to which it is possible to avoid undesirable

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[1] Schorigin, *Ber.*, 40, 3111 (1907); 43, 1931 (1910); Schlubach and *Goes, ibid.*, 55, 2889 (1922); Ziegler and Colonius, Ann., 479, 135 (1930).

[2] Schorigin, Ref. 1; *Ber.*, 41,2723 (1908).

side reactions, and some indications on this point may be had from the known behavior of simple halides. Sodium and n-heptyl bromide at the boiling temperature give tetradecane, 67%; heptane, 9%; heptene, 3%; heneicosane, 3%; hydrocarbons of higher molecular weight, some.[3] Sodium and butyl bromide in ether under specified conditions give *n*-octane, 68%; butane ?, ?%; butene, *ca.* 1.5%; dodecane, *ca.* 0.15%; hexadecane, *ca.* 0.05%.[4] In both these typical cases the principal by-product is probably the hydrocarbon RH. In the reaction of the dihalide, this type of by-product would be identical with one of the normal reaction products. The higher hydrocarbons from butyl bromide and from heptyl bromide are probably not straight chains, and the formation of analogous products from the dihalide would be definitely pernicious because of the difficulty of separating isomeric individuals of high molecular weight. The quoted data on butyl bromide indicate however that in simple Wurtz reactions in ether not more than traces of these higher by-products need be formed.

The action of sodium wire on decamethylene bromide in absolute ether has been studied by Franke and Kienberger.[5] The reaction proceeded smoothly to completion, and the products isolated were: n-decane, 34%; C_{20} hydrocarbon, 30%; a small amount of C_{40} hydrocarbon; and a considerable amount of solid hydrocarbon of higher molecular weight. All of these products were free of halogen. The melting point of the C_{20} hydrocarbon identifies it as n-eicosane. The formation of large amounts of n-decane apparently puzzled Franke and Kienberger, and they repeated their experiments with elaborate precautions to exclude water and alcohol from the solvent and the halide. The results were the same. n-Decane and n-eicosane are, however, strictly normal products of the reaction as it has been formulated above. The fact that Franke and Kienberger could find neither decene nor cyclodecane in the products is worthy of note, for any side reaction would almost certainly be accompanied by the formation of some decene, and any intramolecular reaction by the formation of some cyclodecane. These data indicate that the course of this reaction is, at least for the most part, strictly normal and exclusively intermolecular. The major part of the product is composed of relatively short chains, but this is a matter which may be expected to be susceptible of some control by changes in the experimental conditions, and, as it appears to be in fact, especially by increase in the surface of the sodium.

We had already treated decamethylene bromide in ether with finely divided sodium with stirring before Franke and Kienberger's paper had come to our attention. The product, obtained in good yield, was an ether-in-

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[3] Bachmann and Clarke, THIS JOURNAL, 49, 2089 (1927).

[4] Lewis, Hendricks and Yohe, *ibid.*, 50, 1993 (1928).

[5] Franke and Kienberger, *Monatsh.*, 33, 1189 (1912).

soluble solid, and no material boiling as low as n-decane was present. This product, by extraction and crystallization, was separated into $C_{20}H_{42}$, $C_{30}H_{62}$ and $C_{40}H_{82}$, each fairly pure, representing together about 25% of the total, and a higher fraction, m. p. 108–112°, representing about 75% of the total. This contained 1.39% organic halogen, from which it was freed by heating and stirring it with a small amount of molten sodium in boiling butyl ether. The apparent molecular weight of the resulting hydrocarbon was about 1000. No individuals could be isolated from it by repeated fractional crystallization, and it could not be distilled at 0.1 mm. pressure. It was finally separated into a series of individuals by distillation in the molecular still and by crystallization of the distillates.

Preparation **of the** Hydrocarbon Mixture.—In a 500-cc. flask provided with a reflux condenser and a mercury-sealed mechanical stirrer, **95** g. (**1.52** atoms) of sodium was pulverized under hot xylene. The xylene was removed and replaced by absolute ether, and then **75 g.** (**0.25** mole) of decamethylene bromide was added. The reaction mixture was stirred continuously. It soon developed a deep blue color. It was gently heated for one hour and then allowed to boil without external heating for two and one-half hours. Finally it was heated for two and one-half hours more and then allowed to stand overnight. The excess sodium in the thick mass was decomposed by alcohol, a large volume of water was added, and the mixture was filtered with suction. The only material found in the ethereal layer of the filtrate was **0.5** cc. of an oil boiling at 240–330°. The soft white residue on the funnel liquefied almost completely on being stirred with boiling water and solidified to a crystalline mass on cooling. It weighed **30.5** g. (87.1% calculated as CH_2). It melted from **85** to 100° and contained bromine (found, **2.17**, 2.27%). This solid was heated and vigorously stirred for five hours with **7** g. of molten sodium in boiling butyl ether. The excess sodium was decomposed by alcohol, a large volume of water was added, and the mixture was filtered. The solid residue on the funnel was washed with boiling water and dried. It weighed **21** g. It was free of halogen and melted from **87** to 105°. This is the material which was submitted to fractionation in the molecular still. After the butyl ether had been removed from the non-aqueous layer of the distillate, there remained **6** g. of a soft waxy solid melting at 48–54°.

Separation **of the** Hydrocarbon Mixture.—Eight grams of the solid hydrocarbon, m. p. 87–105°, described above was heated in a small molecular still[6] provided with a water-cooled condenser and a trap cooled with liquid air. The pressure in the system was continually maintained below 10^{-5} mm. Fractions were collected as follows.

Temp. of bath, °C.	Wt. of distillate, g.	M. p. of distillate, °C.
130	0.7	35 – 55
150–160	.27	60 – 75
150–160	.15	60 – 78
150–160	.20	77 – 79
160	.12	78 – 81
180	.20	79 – 84
190	.19	87 – 89

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[6] Washburn, *Bur. Standards* **J. Research, 2,476 (1929).**

Temp. of bath, °C.	Wt. of distillate, g.	M. p. of distillate, °C.
195	.08	87 - 91
195	.10	90 - 90.5
200–220	.52	90.6– 92
250	31	94.5– 97
250	.11	96 - 98
250	.20	97 - 99.5
250	.10	98 –100.5
250	.05	99 –101
250	.08	99 –102
300	.47	103 –105
300	.17	103 –106.5
Total	4.02	
Residue	3.16	
Loss	0.82	

The loss is due to the impossibility of quantitatively removing the distillate from the condenser. In this distillation the average area of the evaporating surface was about 18 sq. cm. About twenty hours was required for the collection of each of the above listed fractions. When the temperature of the heating bath was raised above 300° with the view of distilling the residue, the pressure rose and no distillation could be effected.

The distillates were grouped together into eight fractions and redistilled. The rate of distillation from these partially purified materials was very much higher than from the initial mixture. The distillates were crystallized to constant melting points. The properties of all the fractions thus obtained are indicated in Table I.

TABLE I

INDIVIDUAL HYDROCARBONS

Hydrocarbon	M. p. found, °C.	Solvent used for crystallization	Distn. temp., °C.	Anal. calcd.		Anal. found	
				C	H	C	H
$C_{20}H_{42}$	35 - 35.6	Abs. EtOH	60°	85.00	15.00	85.45	15.03
$C_{30}H_{62}$	65 - 66	Abs. EtOH + Et_2O	100	85.21	14.79	85.28	14.45
$C_{40}H_{82}$	80.5– 81	Ethylene chloride	150	85.31	14.69	85.59	14.74
$C_{50}H_{102}$	91.9– 92.3	Ligroin + petroleum ether	200	85.37	14.63	85.34	14.53
$C_{60}H_{122}$	98.5– 99.3	Butyl acetate	250	85.41	14.59	85.66	14.34
$C_{70}H_{142}$	105 –105.5	Butyl acetate	300	85.44	14.56	85.50	14.58
Soluble residue	110 –114	Butyl acetate	Not distillable				

Identity **and** Properties of the Hydrocarbons.—The melting points 36.7°[7] and 65.6–66°,[8] respectively, have been assigned to n-eicosane and

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[7] Krafft, *Ber.*, 19, 2220 (1886). The C_{20} hydrocarbon of Franke and Kienberger (Ref. 5) which melted at 36° was unquestionably n-eicosane; and their C_{40} hydrocarbon, which melted at 72°, was probably a mixture of n-triacontane and n-tetracontane.

[8] Gascard, Ann. *chim.*, [9] 15,332 (1921); Peterson, *Ber.*, 12,741 (1879).

n-triacontane, and these values are in good agreement with our observations. The other four hydrocarbons listed in Table I are all new, and the last one stands six atoms above any paraffin previously described. Several intermediate members of this same series have been described, however, and from the available data it is possible to construct a smooth curve of melting points covering the range C_{18}–C_{70}. The usefulness of such a curve in estimating the most probable values for individual hydrocarbons has already been emphasized,[9] and in the curve presented in Fig. 1 the crosses are Hildebrand and Wachter's estimates of the best values for hydrocarbons in the range C_{19}–C_{36}. We have used a method of plotting similar to that suggested by Austin[10] and have included the values for the three previously known hydrocarbons above $C_{36}H_{74}$. These are $C_{54}H_{110}$, $C_{62}H_{126}$ and $C_{64}H_{130}$, all described by Gascard.[8] Our data and those of Gascard fall very close to the same smooth curve which fits the best data for the lower hydrocarbons, and this fact incidentally affords confirmation of Hildebrand and Wachter's contention that the melting points accepted by the "International Critical Tables" for some of the hydrocarbons in the range C_{24} to C_{32} are much too high.

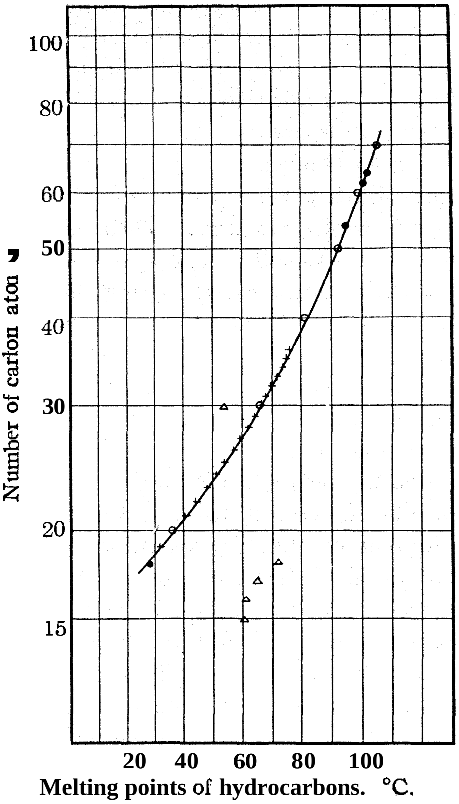

Fig. 1.—Normal paraffins: ●, Gascard, Ann. *chim.*, [9] 15,332 (1921); +, Hildebrand and Wachter, THIS JOURNAL, 51, 2487 (1929); O, new data. Cyclopolymethylenes: △, Ruzicka and co-workers, *Helv. Chim. Acta*, 9, 499 (1926); 11,496 (1928).

Hell and Haegele described dimyricyl in 1889[11] and ascribed to it the formula $C_{60}H_{122}$. This ascription acquired the sanction of recognition by Beilstein (third and fourth editions) and remained unquestioned until evidence that the myricyl radical contains 31 carbon atoms appeared. In 1921 Gascard[8] concluded that Hell and Haegele's hydrocarbon was $C_{62}H_{124}$ and that hexacontane had never been prepared. Our data confirm this

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[9] Hildebrand and Wachter, THIS JOURNAL, [9] 51,2487 (1929).

[10] Austin, *ibid.*, 52,1049 (1930).

[11] Hell and Haegele. Ber., 22,502 (1889).

conclusion. Hexacontane melts at 98.5 to 99.3°, while the observed melting points ascribed to dimyricyl have ranged from 100.5–102°.

Independent proof of the identity of the six hydrocarbons is furnished by x-ray diffraction patterns which have been obtained by Dr. A. W. Kenney and will be described in a separate publication.

Melting point data are available for only five cyclic polymethylenes above C_{10}. These fragmentary data do not fall on any smooth curve (see Fig. 1), but they are all widely enough separated from the data for the normal paraffins to provide additional assurance that none of our paraffin compounds are cyclic.

Under the heading distillation temperature in Table I are listed the minimum bath temperatures required to effect evaporation at a moderate rate in the molecular still. These temperatures are quite characteristic since they are, in each case, only a few degrees above the temperatures at which no distillation occurs. Using the Langmuir formula[6] it is possible to make a rough calculation of the order of magnitude of the vapor pressures of these hydrocarbons from the minimum distillation temperatures. Such calculations indicate a value less than 0.01 mm. for heptacontane at 300° and a value less than 1 mm. for triacontane at 100°. Heptacontane has a molecular weight of 983, and it is probable that no organic compound of much higher molecular weight than this can ever be distilled under any experimental conditions however favorable. The residue remaining from the removal of the heptacontane undoubtedly contained some octacontane, but none of this distilled out at a bath temperature of 300° and when the temperature was raised higher than this, decomposition set in. This experimental result agrees remarkably well with the inferences to be drawn from the data presented by Meyer and Dunkel.[12] From these data one can calculate that the molecular cohesion of heptacontane will be about 71,000 calories and that of octacontane about 81,000 calories. Since the heat of separation of the carbon-carbon bond is about 75,000 calories, it should be possible to distil the first of these compounds, but not the second. Saturated paraffins have, in general, a lower molecular cohesion for a given molecular weight than any other types of compounds, and hence the limit of distillability will be found at a lower molecular weight for other compounds than hydrocarbons. These results are also in agreement with data of a different kind presented by Burch[13] who, by distilling a Pennsylvania petroleum in a molecular still, obtained as the highest distillable fraction a material having an apparent average molecular weight of 801 and a residue of apparent molecular weight of 1550.

The physical properties of n-heptacontane are similar to those ascribed to dohexacontane and tetrahexacontane. It is very slightly soluble in

[12] Meyer, *Naturw.*, 16, 781 (1928); Dunkel, *Z. physik. Chem.*, 138, 42 (1928).

[13] Burch, Proc. *Roy. Soc.* (London), 123, 271 (1929).

boiling alcohol, ether or petroleum ether, but crystallizes well in the form of minute needles from hot butyl acetate or benzene. It dries to a starch-like powder which has a great tendency to become electrified.

It was hoped that it might be possible to isolate hydrocarbons much higher than heptacontane, since information concerning simple individuals of very high molecular weight would be of great importance to the study of macromolecular materials generally, but there seems little probability of achieving this result without some change in method or advance in technique. The residue from which the n-heptacontane was distilled is a mixture which undoubtedly contains n-octacontane, n-nonacontane, n-decacontane and still higher hydrocarbons. It is readily soluble in hot butyl acetate (except for a trace of insoluble and infusible material), and it separates as a powder melting at 110–114°. Its apparent average molecular weight in boiling benzene is about 1300. (Calcd. for $C_{90}H_{182}$, 1263.) By extraction with hot ethylene chloride, it was separated into fractions melting at 100–107°, 106–111° and 110–114°. In a sense this mixture is a polymeric homologous series, but its solubility is much lower than that of such supposedly analogous series of higher molecular weight as polystyrene and hydro-rubber. It resembles a probably similar but more complex mixture of hydrocarbons obtained by Fischer and Tropsch by the catalytic hydrogenation of carbon monoxide.[14]

There is one point bearing on the behavior of highly polymeric materials which is capable of a rough preliminary test with the series of hydrocarbons described above. It has been suggested[15] that the apparent decrease of molecular weight (decrease of viscosity, etc.), which is observed when rubber and other very high polymers are gently heated or treated with certain mild chemical agents or subjected to mechanical stresses, is real and is due to the fact that the thermal stability of molecules decreases continuously with increasing size, and in these materials has reached so low a value that cracking occurs at slightly above room temperature. Samples of each of the hydrocarbons from C_{30} to C_{70} were sealed off in small bulbs under nitrogen and heated side by side in a metal-bath After five minutes at 400° all the melting points were unchanged. After five minutes at 410° the melting point of C_{70} was lowered from 106–107° to 104–105°. The melt, moreover, was not clear as before but turbid. The turbidity disappeared rather sharply at 110°—like a liquid crystal. The melting points of the other hydrocarbons were substantially unchanged, but, except for C_{30}, they all gave hazy melts which cleared up only at temperatures somewhat above their true melting points. After five minutes more at 420° all the melting points had become lower (that of C_{70} most) and there was some coloration. The C_{30} was white, the C_{40} was cream-colored, and the higher hydrocarbons

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[14] Fischer and Tropsch, *Brennstoff-Chemie*, *8*, 166 (1927).

[15] Staudinger. Ber., *59*, 3037 (1926).

in regular order were increasingly darker. When the tubes were finally opened after five minutes more at each of the temperatures 430, 450 and 470°, they were found to contain considerable gas—most above the C_{70} and least above the C_{30}. Thus, the decrease in thermal stability with increasing molecular weight which is so marked in passing from methane (*ca.* 700°)[16] to ethane (*ca.* 550°),[17] and from ethane to hexadecane (*ca.* 470°)[18] is still detectable in going from triacontane to heptacontane, but it has already fallen to such a small value that it would be somewhat unsafe to infer that a paraffin hydrocarbon of molecular weight 200,000 or even greater might not persist at room temperature.

Mechanism of the Action of Sodium on Decamethylene Bromide.—It has already been pointed out that all the observed products of this reaction are accounted for by assuming replacement of the bromine atoms of the halide by sodium, and the subsequent coupling of this with other molecules of the halide, or its reaction with the solvent. The absence of cyclic hydrocarbons is not surprising since, although the higher cycloparaffins are no less stable than cyclohexane,[19] the formation of large rings in bifunctional reactions occurs only under very exceptional conditions.[20] In the formation of esters from ω-hydroxy acids, amides from amino acids, and anhydrides from dibasic acids, intramolecular reaction occurs exclusively only if there is a possibility of forming a 5- or a 6-membered ring. The behavior of alkylene halides toward metals however is peculiar in that there seems to be little tendency toward intramolecular reaction even when a 5- or a 6-membered ring might be formed. Thus the action of magnesium on alkylene halides leads to considerable coupling, but even from pentamethylene halides no cyclic hydrocarbon is formed.[21] This suggests that the coupling perhaps occurs largely at the metal surface where the atoms at the ends of the chains may be fixed by forces of adsorption and their freedom of intramolecular approach hindered.

Our main objective in the experiments described above was to prepare normal paraffins of very high molecular weight, and we made a number of attempts to adjust the experimental conditions so as to increase the length of the reaction chains. We treated decamethylene bromide with molten sodium in boiling butyl ether, with liquid sodium–potassium alloy in ethyl ether, with molten sodium in boiling octane and with finely divided sodium in the absence of a solvent. There was no evidence of the formation of considerable amounts of paraffins higher than C_{100} in any of these experi-

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[16] Bone and Wheeler, J. *Chem. Soc.*, 81,542 (1902).

[17] Williams-Gardner, *Fuel Science Practice*, 4,430 (1925).

[18] Gault and Hessel, *Ann. chim.*, [10] 2,319 (1924).

[19] Ruzicka and co-workers, *Helv. Chim. Acta*, 9,499 (1926); 11,496 (1928).

[20] Carothers, THIS JOURNAL, 51,2548 (1929); and subsequent papers of this series.

[21] Zappi, *Bull. soc. chim.*, [4] 19, 249 (1916); v. Braun and Sobecki, *Ber.*, 44, 1918 (1911).

ments. We also prepared decamethylene dimagnesium bromide and treated it with cupric chloride in the expectation that products of the formula $BrMg[(CH_2)_{10}]_xMgBr$ would be formed. The chief product (71%), however, after the addition of water, was a volatile liquid apparently chiefly composed of decane and decene. The amount of higher boiling material (20%) did not exceed that which would arise from the coupling products usually produced in the formation of such reagent.: as decamethylene dimagnesium bromide.[21]

Preparation of Decamethylene Bromide.—The preparation, in good yields, of a whole series of polymethylene bromides from the glycols via the esters of the corresponding dibasic acids has been described by Chuit[22] but without great experimental detail. We first attempted to reduce ethyl sebacate by Levene and A len's modification[23] of the original Bouveault procedure.[24] In this modification, which has given good results in the reduction of esters of monobasic acids, the sodium is first granulated by stirring in hot toluene, and the reaction mixture is vigorously stirred during the addition of the alcohol–ester mixture. This procedure gave very poor yields of decamethylene glycol; the yields were increased by diminishing the speed of stirring and became quite good when the stirring was omitted altogether. The procedure finally adopted was almost identical with that of Bouveault, and the details are given below.

A condenser having a length of 2 meters and an inside diameter of about 2.5 cm. is connected with the side neck of a 5-liter two-necked round-bottomed flask, and the central neck of the flask is provided with a 1-liter dropping funnel. One hundred and fifteen grams (5 atoms) of sodium in a single piece or in two or three large pieces is placed in the flask. One hundred and twenty-nine grams (0.5 mole) of ethyl sebacate is dissolved in one liter of thoroughly dried absolute ethyl alcohol and poured into the dropping funnel. One hundred and fifty to two hundred cubic centimeters of the alcohol–ester mixture is allowed to fall onto the sodium at once. After two or three minutes the reaction becomes vigorous and the sodium melts. As soon as the sodium has melted another portion (about 100 cc.) of the alcohol–ester mixture is suddenly added. This causes the molten sodium to break up into fine particles, and the reaction becomes much more vigorous. The rest of the alcohol–ester mixture is then added as rapidly as possible (five to six minutes). As soon as the vigor of the reaction has somewhat subsided, the flask is heated by an oil-bath to 110–115° until most of the sodium has dissolved. The ethyl alcohol is then removed from the reaction mixture by steam distillation, and the glycol is removed from the residue by extended (about seventy-two hours) continuous extraction with ether. The glycol is purified by distillation. The combined yield from nine such runs was 593 *g.* or 75% of the theoretical.

Continuous ether extraction as a means of isolating glycols produced by the reduction of esters has been successfully used by C. S. Marvel;[25] otherwise the above pro-

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[22] Chuit, *Helv. Chim. Acta*, **9**, 264 (1926); Chuit and Hauser *ibrd.*, 12, 850 (1929).

[23] Levene and Allen, *J. Biol. Chem.*, 27, **443** (1916); cf Adams and Marvel, *Univ. Illinois Bull.*, **20**, 50 (1922).

[24] Bouveault and Blanc, Bull. *soc. chim.*, [3] **31**, 666 (1904).

[25] Private communication.

cedure is similar to that which has also been used by Miiller for preparing a series of glycols.[26]

Using the method described by Chuit,[22] we obtained from decamethylene glycol only a 70% yield of bromide and this was contaminated with bromohydrin. The following modification of this method gave a purer product and a better yield.

Dry hydrogen bromide was led into a well-stirred melt of 255 g. (1.47 moles) of decamethylene glycol in an open flask until the mass was saturated. The temperature of a metal-bath surrounding the flask was kept at 90–95°. After saturation was complete the bath temperature was raised to 135–140° and a slow stream of hydrogen bromide was led in for six hours. The reaction mass was then cooled, diluted with benzene and decanted from a small amount of water remaining in the flask. The benzene was then removed by distillation, and the product distilled under diminished pressure; yield, 376 g. (85.5%); b. p., 168–172° (10 mm.).

Anal. Calcd. for $C_{10}H_{20}Br_2$: Br, 53.33. Found: Br, 53.16, 53.16.

We are indebted to Mr. W. L. McEwen for the preparation of decamethylene glycol.

Summary

By the action of sodium on decamethylene bromide in ether a mixture of paraffins of the general formula $H—[(CH_2)_{10}]_x—H$ has been prepared. By fractional distillation in the molecular still and by crystallization, the following individuals have been isolated from this mixture: n-eicosane, n-triacontane, n-tetracontane, n-pentacontane, n-hexacontane, *n*-heptacontane. The last four of these are new, and the last one has a higher molecular weight than any pure paraffin hydrocarbon hitherto described. The residue remaining from the separation of the hydrocarbons named amounts to about 25% of the total and is composed of still higher members of the same series which it has not yet been possible to separate. The mechanism of the reaction and the properties of the products are discussed.

WILMINGTON, DELAWARE

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[26] Miiller, *Monatsh.*, 49, 27 (1928).

[CONTRIBUTION NO. 42 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

STUDIES ON POLYMERIZATION AND RING FORMATION. VIII. AMIDES FROM a-AMINOCAPROIC ACID

BY WALLACE H. CAROTHERS AND GERARD J. BERCHET

RECEIVED OCTOBER 9, 1930 PUB ISHED DECEMBER 18, 1930

ε-Aminocaproic acid on being heated reacts with itself and yields two products—the corresponding 7-membered lactam, 20–30%, and an undistillable material of approximately the same composition, 80–70%.[1] The following related facts are of interest. δ-Aminobutyric acid and a-aminovaleric acid readily lose water and yield the corresponding 5- and 6-membered lactams.[2] No corresponding polymers are formed or known. The reaction of ζ-aminoheptoic acid with itself is apparently exclusively intermolecular, for it leads to an undistillable product quite different in its properties from the known &membered lactam.[3] Similar relationships are found among the hydroxy acids: y- and 6-hydroxy acids yield lactones; ε-hydroxy acids yield both lactones and polyesters,[4] and the higher w-hydroxy acids yield only the polyesters,[5] although many of the higher lactones are known.[6] Polyesters have now been studied in some detail,' but (except for polypeptides) little attention has been devoted to the polyamides. In this paper we record some observations concerning the polyamide derived from E-aminocaproic acid.

Water is rapidly evolved when E-aminocaproic acid is heated above its melting point (*e.* g., to 210–220°). The polymer and the lactam which result are readily separated by allowing the latter to distil under diminished pressure, or by extracting it with boiling alcohol. In different experiments the yield of lactam was 20–30% and the polymer 80–70%. The same products were obtained by gradually heating the ethyl ester of the acid from 160 to 200° during six hours, and the yield of lactam was about 38%.

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[1] V. Braun, *Ber.,* 40, 1840 (1907); Gabriel and Maas, *ibid.,* 32, 1266 (1899)

[2] Gabriel, *ibid.,* 22,3338 (1889); Schotten, *ibid.,* 21,2240 (1888).

[3] V. Braun, *ibid.,* 40, 1834 (1907); Wallach, *Ann.,* 312, 205; 309, 18 (1899); Manasse, *Ber.,* 35,1367 (1902).

[4] Baeyer and Seuffert, *ibid.,* 32, 3619 (1899); Blaise and Koehler, *Compt. rend.,* 148,1772 (1909); Marvel and co-workers, THIS JOURNAL, 46,2838 (1924).

[5] (a) Blaise and Koehler, Ref. 4; (b) Chuit and Hauser, *Helv. Chim. Acta,* 12, 4634 (1929); *(c)* Lycan and Adams, THIS JOURNAL, 51,625,3450 (1929); (d) Blaise and Marcilly, *Bull. soc. chim.,* 31,308 (1904).

[6] Ruzicka and Stoll, *Helv. Chim. Acta, 11,* 1159 (1928).

[7] (a) Lycan and Adams, THIS JOURNAL, Ref. 5c; (b) Carothers and Arvin, *ibid.,* 51,2560 (1929); (c) Carothers and Van Natta, *ibid.,* 52,314 (1930); (d) Carothers and Dorough, *ibid..* 52,711 (1930); (e) Carothers, Dorough and Arvin, *ibid.,* 52,3292 (1930); (f) Chuit and Hauser, Ref. 5b; *(g)* Blaise and Marcilly, Ref. 5d; (h) Bougault and Bourdier, *J. pharm. chim., [6]29,* 561 (1909); [6] 30, 10 (1909).

The polymer is a hard gray wax, insoluble in most organic solvents, but soluble in hot formamide, from which it separates as a microcrystalline powder melting at 212–214°. Its analytical composition agrees very closely with that required for the structural unit $—NH—(CH_2)_5CO—$.

Anal. Calcd. for $C_6H_{11}ON$: C, 63.71; H, 9.73. Found: C, 63.35, 63.62; H, 9.93, 10.07. A product from another preparation gave: C, 63.35, 63.45; H, 9.56, 9.43.

It is quantitatively hydrolyzed in six hours by boiling concentrated hydrochloric acid to ϵ-aminocaproic acid (identified by conversion to the *p*-toluenesulfonyl derivative, melting point and mixed melting point, 105–106°).

By partial hydrolysis, polyaminocaproylaminocaproic acids are formed. Thus, a sample of the polyamide was heated to boiling for one hour in concentrated hydrochloric acid solution, and the solution was diluted with water to precipitate the unchanged polymer (about 50%). The material remaining in solution, on being treated with alkali and *p*-toluenesulfonyl chloride, gave a solid product which, after repeated crystallization, showed a neutral equivalent corresponding with the formula C_7H_7-SO_2-$[NH(CH_2)_5CO]_3$-$NH(CH_2)_5COOH$ (calcd., 607; found, 601). The structure of the polymer may, therefore, be represented by the formula

$$? —NH(CH_2)_5CO—[NH(CH_2)_5CO]_x—NH(CH_2)_5CO— ?$$

It is a true condensation polymer and is formed directly from the amino acid by intermolecular reaction. This is proved by the fact that the lactam does not polymerize under the conditions of formation of the polyamide either in the presence or absence of catalysts. Moreover, no lactam can be obtained from the polyamide by heating it to high temperature in high vacuum. Thus there is no such reversible relationship between lactam and polyamide as is found[7c,e] to exist between six-membered cyclic esters and corresponding polyesters. Lactam and polyamide result from the amino acid by two independent and simultaneous processes. The lactam incidentally is really the 7-ring $\underline{\ulcorner NH(CH_2)_5CO \urcorner}$.[8] This was proved by identifying its hydrolytic product with e-aminocaproic acid through its *p*-toluenesulfonyl derivative by means of a mixed melting point.

The polyamide is sufficiently soluble in phenol to permit a determination of molecular weight by cryoscopy. Values obtained ranged from 800 to 1200, and since the errors of this method are such as to lead to low results it may be assumed that at least 10 molecules of the amino acid must have participated in the formation of a single molecule of the polyamide.

The question of the nature of the groups at the ends of the polyamide

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[8] The shifting of a functional group down a chain in attempts to prepare large rings by bifunctional reactions has been reported by various investigators. See, for example. Blaise and Koehler, Ref. 4.

chains cannot yet be answered. The formation of large rings is very improbable on theoretical grounds,[9] and in the formation of polyesters ring formation is known not to occur—the hydroxyl or carboxyl groups still persist at the ends of the polyester chain.[7b,c,d,5c] However, no certain evidence of the presence of terminal amino or carboxyl group in the molecule of the polyamide could be obtained. The polyamide dissolves readily in cold concentrated hydrochloric acid, but when the solution is diluted with water it separates unchanged and free from more than traces of halogen. It is not soluble in hot or cold aqueous sodium hydroxide nor does it form any sodium salt. It reacts with molten *m*-bromobenzoic anhydride and, in hot pyridine, with *p*-bromobenzene-sulfonyl chloride. The products contain bromine in amounts which correspond with derivatives of minimum molecular weights about 1100 and 1500, respectively, but in view of the failure of other reactions these cannot be accepted as evidence of the presence of free amino groups in the polyamide. At present we are inclined to assume that the amino and carboxyl groups which would normally be present at the ends of the polyamide chains are lost by pyrolysis. (The evolution of carbon dioxide during the formation of the polyamide could not be detected, but the vapors evolved had a strong amine odor.)

Summary

ε-Aminocaproic acid (or its ethyl ester) on being heated reacts with itself both intra- and intermolecularly and yields the 7-ring lactam (*ca.* 30%) and a polyamide (*ca* 70%). The formation of a molecule of the latter probably involves at least ten molecules of the amino acid.

WILMINGTON, DELAWARE

NOTES

A Method for the Determination of Molecular Weights in Liquid Ammonia.—Very recently Schwarz[1] and Signer[2] have published a new method for the determination of molecular weights. This method makes use of the principle that two solutions in the same solvent confined with a common vapor phase will come to the same molecular concentration by diffusion of the vapor.

The advantages of the method are that it enables the molecular weights of substances of low solubility and large molecular weight to be determined accurately; it makes possible molecular weight determinations in the same solvent at different temperatures; and it is adaptable to micro-manipulation.

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[9] Carothers, THIS JOURNAL, 51, 2556 (1929).

[1] Schwarz, *Monatsh.*, 53, 54, 926 (1929).

[2] Signer, *Ann.*, 478, 246 (1930).

Before these publications appeared, we found, employing the same method, that the slow diffusion of organic solvents was a great disadvantage. To correct this fault we resorted to liquid ammonia as solvent and found that it gave excellent results.

Even with liquid ammonia the time required to reach equilibrium was about 150 hours. The rate of transfer varied from 0.1 to 1.0 cc. per day, depending on the differences in concentrations of the solutions.

Apparatus and Procedure.—The apparatus was made by joining two long calibrated test-tubes with a U-tube at their middle points. The tubing was 1 mm. thick and 8 mm. in internal diameter. Into the U was sealed a 4-mm. tube by which connection was made with the ammonia cylinder. Known quantities of solutes were placed in the calibrated tubes, ammonia introduced and the tubes sealed.[3] The apparatus, with U-tube inverted, was rocked mechanically until equilibrium was attained. The final volumes of the solutions were then read and the molecular weight of the unknown calculated from the formula, $M_2 = (w_2v_1M_1)/(w_1v_2)$. The symbols M, v and w signify molecular weight, final volume and solute weight, respectively. The subscripts 1 and 2 refer in turn to the standard and unknown substances.

Data and Discussion.—The results obtained are summarized in Table I.

TABLE I

MOLECULAR WEIGHTS IN LIQUID AMMONIA

Expt.	Unknown	Wt., g.	Volume Initial	Volume Final	Standard	Wt.	Volume Initial	Volume Final	Mol. wt. Obs.	Mol. wt. Calcd.
1	Resorcinol	0.495	8.67	8.52	Resorcinol	0 450	7.50	7.64	108	110
2	Resorcinol	.495	10.95	8.68	Resorcinol	.450	6.23	7.52	105	110
3	Mannitol	.231	10.33	8.53	Mannitol	.300	9.57	11.33	186	182
4	Mannitol	.231	6.91	8.57	Mannitol	.300	12.91	11.33	185	182
5	Valeramide	.386	9 20	8.55	Valeramide	.429	8.77	9.28	99	101
6	Ammonium chloride	.386	11.11	12 22	Ammonium chloride	.384	14.52	13.42	59	53.5
7*	Thymol	.125	6.48	6.18	Thymol	.141	6.34	6.62	142	150
8*	Thymol	.193	8.23	5 39	Resorcinol	.264	7.65	10.46	156	150
9	Thymol	.268	7.79	4.85	Resorcinol	.340	4.43	7.37	132	150
10	Thymol	.231	6.82	5.14	Resorcinol	.209	6.40	8.09	191	150
11	Diphenylamine	.390	8.43	5.83	Resorcinol	.360	7.72	10.28	210	169
12	Ammonium chloride	.263	7.32	5.91	Resorcinol	.500	8 05	9 40	92	53.5
13*	Ammonium chloride	.325	8.18	9.15	Resorcinol	.307	8.30	7.38	94	53.5
14	Valeramide	.457	5.63	7.73	Diphenylamine	.468	6.40	4.35	93	101
15	Thymol	.169	8.27	8.47	Diphenylmine	.142	7.88	7.63	181	150

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[3] Franklin has described the technique used for handling the liquid ammonia, *J. Phys. Chem.*, 15, 509 (1911).

TABLE I (*Concluded*)

			Volume				Volume		Mol. Wt.	
Expt.	Unknown	Wt., g.	Initial	Final	Standard	Wt.	Initial	Final	Obs.	Calcd.
16	Diphenylamine	0.156	8.58	7.82	Mannitol	0.240	8.18	8.78	133	169
17	Resorcinol	.353	7.44	8.48	Mannitol	.498	7.81	6 75	103	110
18*	Thymol	.148	7.81	5.54	Mannitol	.288	7 56	9.72	164	150
19*	Naphthalene	.180	6.00	6.49	Mannitol	.177	5.54	4.90	140	128
20*	Sorbitol	.209	6.10	5.69	Mannitol	.276	6 05	6.46	157	182
21*	Mannose	.191	11.16	10 00	Mannitol	.301	11.44	12.44	144	180
22*	Fructose	.348	11.38	15 31	Mannitol	.299	10.67	6.61	92	180
23*	a-Methyl glucoside	.228	8.04	7.68	Mannitol	188	7.19	7.44	214	212

The data in the table show what accuracy may be expected by the use of this method. Undoubtedly more accurate results can be obtained if the tubes be put in a constant temperature bath, for better results were obtained in a room where the temperature variation was not more than 2° (starred experiments) than in the laboratory where the variations were much greater (unstarred experiments).

That the method is correct in principle is shown by the results recorded in Expts. 1–7. Here the solutions contained the same solute and reached the same molecular concentrations.

A surprising result was discovered in the case of ammonium chloride. Experiments 12 and 13 indicate that this substance exists in the dimolecular form in liquid ammonia.

The low value obtained for fructose (Expt. 22) is probably due to its reaction with the solvent. That such reaction is likely follows directly from Strain's[4] results obtained with other ketones.

Should a micro method for molecular weight determinations in liquid ammonia be desirable, this method can probably be micrified, because Schwarz[1] has shown that this type of method is adaptable to micromanipulation.

The writers are indebted to Dr. F. W. Bergstrom and the Department of Chemistry of Stanford University for the liquid ammonia required for this investigation.

DIVISION OF PLANT BIOLOGY
CARNEGIE INSTITUTION OF WASHINGTON
STANFORD UNIVERSITY, CALIFORNIA

HAROLD H. STRAIN
JAMES H. C. SMITH

RECEIVED SEPTEMBER 12, 1930
PUBLISHED DECEMBER 18, 1930

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[4] Strain, THIS JOURNAL, 52,820 (1930); *ibid.*, 52,1216 (1930).

ω-Alkylalkoxyaminopropiophenones.—It has been shown by Mannich that condensation takes place between ketones, formaldehyde or trioxymethylene and amine hydrochlorides with the formation of β-keto bases.[1] Later he found that the β-keto bases which were formed by the condensation of alkyl aryl ketones with formaldehyde and primary or secondary amines possessed local anesthetic action.[2]

It has been shown that substituted O-alkylhydroxylamines, in general, have the physiological properties of the amines to which they are related.[3] It therefore seemed probable that w-alkylalkoxyaminopropiophenones would be local anesthetics. It has been found, however, that these compounds exhibit only very slight anesthetic action, at least when they are applied to the mucous membrane of the tongue. They were synthesized by the method of Mannich.

One molecular equivalent each of acetophenone and O,N-dialkylhydroxylammonium chloride, two molecular equivalents of trioxymethylene and ten molecular equivalents of absolute alcohol were refluxed for twenty-four hours. The solution was cooled and dry ether was added. The precipitate which formed was dissolved in water and the aqueous solution was extracted with ether in order to remove any trace of acetophenone. Caustic alkali was then added to the solution of the hydrochloride in water. The oil which separated was extracted with ether and the ether solution dried with sodium sulfate. After the ether had been distilled off an oil remained which was distilled in *vacuo*.

w-Methylmethoxyaminopropiophenone was a colorless oil, b. p. (23 mm.) 159"; yield, 50%

Anal. *Calcd.* for $C_{11}H_{15}O_2N$: N, 7.25. Found: N, 6.95.

w-Ethylethoxyaminopropiophenone was a colorless oil, b. p. (9 mm.) 151–153"; yield, 18%.

Anal. $C_{13}H_{19}O_2N$: N, 6 34. Found: N, 6.61.

In order to prepare the hydrochloride of ω-methylmethoxyaminopropiophenone, dry hydrogen chloride was passed into a solution of the base in dry ether. A white precipitate formed which was dissolved in warm chloroform and reprecipitated with ether in order to completely purify it; m. p. 155°.

Anal. Calcd. for $C_{11}H_{16}O_2NCl$: Cl, 15.44. Found: Cl, 15.19.

CONTRIBUTION FROM THE
FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

RANDOLPH T. MAJOR

RECEIVED OCTOBER 29, 1930
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[1] Mannich, *Arch. Pharm.*, 255, 261 (1917); Mannich and Braun, *Ber.*, 53, 1874 (1920).

[2] German Patent 379,950; *Friedländer*, 14, 1246.

[3] Jones and Major, THIS JOURNAL. 49,1527 (1927).

COMMUNICATIONS TO THE EDITOR

THE "STAR TRAIL" METHOD FOR THE SPECTROGRAPHIC QUANTITATIVE DETERMINATION OF THE ELEMENTS

Sir:

Diligent search of the voluminous literature has failed to disclose the "Star Trail" method for the spectrographic quantitative determination of the elements as described below. A bright line is isolated from a spectrum by interposing a slotted light stop between the refracting element and the telescope of a spectroscope. The image of the line so isolated falls upon a film affixed to a rapidly rotating drum which spreads out this line into a band. The rotation serves to equalize any flickering due to any cause and to render the band of uniform density, which depends upon the concentration of the given element in the solution employed and upon the time during which the film is exposed to the light. The drum carrying the film can be racked up or down so as to expose different parts of the film, as desired.

Spectra due to different concentrations of the same element, employed as standards, are exposed in a series with the unknown concentration on the same film as a succession of bands, keeping time of exposure and speed of rotation of the film as constants. The bands of different density can be compared directly by cutting the film across all the bands and bringing the latter into direct alignment. Density can also be controlled by the manner of developing the film.

Experiments with sodium chloride in concentrations varying between 0.500 and 0.0250% and exposure of five minutes to a portrait panchromatic film gave satisfactory indications of the value of the method.

Work is now proceeding at the University of Illinois with special reference to the application of the method to the quantitative analysis of the alkali metals.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

A. C. SHEAD
G. FREDERICK SMITH

RECEIVED OCTOBER 10, 1930
PUBLISHED DECEMBER 18, 1030

THE PARACHORS OF TWO ISOMERIC CHLORODINITROBENZENES

Sir:

In a recent communication[1] Sickman and Menzies reported the results of a determination of the parachor of 1-chloro-3,4-dinitrobenzene from surface tension measurements at 40 to 60°. This was found to be approximately the same, allowing for "drift of parachor with temperature," as that evaluated from Jaeger's measurements[2] of the surface tension of the

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[1] Sickman and Menzies, THIS JOURNAL, 52, 3327 (1930).

[2] Jaeger, *Z. anorg. allgem. Chem.*, 101, 117 (1917).

1-chloro-2,4-dinitro isomer at 60 to 95°. After pointing out that in both these cases the observed parachor is more than 3% lower than that calculated from Sugden's atomic and structural constants,' the authors added, "the latter have been recalculated by Mumford and Phillips." By using these newer constants, the discrepancy is not diminished.. ..." As will be apparent from the following table, however, this statement is incorrect, for the use of the reëvaluated constants materially reduces the difference between calculated and observed values.

TABLE I

PARACHORS OF THE CHLORODINITROBENZENES

Compound	Parachor
1-Chloro-3,4-dinitrobenzene (Sickman and Menzies 40 to 60°)	347.4
1-Chloro-2,4-dinitrobenzene (Jaeger 60 to 95°)	348.2
Calculated for either compound (Sugden)	358.3
Calculated for either compound (Mumford and Phillips)	353.2

The latter value, which was, incidentally, quoted in our original paper on the reevaluation[6] is the algebraic sum of the constants for the constituent atoms (*viz.*, 6 of carbon, 3 of hydrogen, 1 of chlorine, 2 of nitrogen and 4 of oxygen), and those for the various structural features (*viz.*, 1 six-membered ring, 5 non-polar and 2 semi-polar double bonds) together with the *appropriate* strain constants, in this case one of -3 units associated with each of the nitro groups, and a complex one of $-(3.4 + 2.4 + 2.2) = -8$ units due to the unsymmetrical accumulation of three negative groups around the benzene nucleus.

It must be noted further that in the case of Jaeger's data for 1-chloro-2,4-dinitrobenzene, only three measurements at lower temperatures have been utilized by Sickman and Menzies. A considerably higher mean parachor is obtained if the other six determinations are also taken into account, as has been done in Table II.

TABLE 11

JAEGER'S DATA FOR 1-CHLORO-2,4-DINITROBENZENE

Temp., °C.	Surface tension. dynes/cm.	Density	Parachor
60.4	45.5	1.515	347.2
76.2	43.9	1.497	348.2
95	42.2	1.477	349.4
114	40.4	1.455	350.9
136	38.3	1.432	351.8
155.1	36.4	1.412	352.3
175.5	34.5	1.391	352.8
190	32.9	1.378	351.9
204.2	31.5	1.365	351.5

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[3] Sugden, J. *Chem. Soc.*, 125, 1177 (1924).

[4] Mumford and Phillips, *ibid.*, 2112 (1929).

[5] Mumford and Phillips, Ref. 4, Table V, p. 2118.

The average of all the measurements is 350.7, but as the parachor rapidly attains and maintains a mean value of about 351.6, it is evident that this should be taken as representative of the compound in question, and the values in the vicinity of the melting point regarded as anomalous. This value, which was quoted in our original paper as the observed parachor of 1-chloro-2,4-dinitrobenzene, is less than 0.5% lower than that calculated from our reevaluated constants, namely, 353.2, and it would, therefore, seem unnecessary to look further for the cause of the apparent discrepancy.

In the case of the 1-chloro-3,4-dinitro isomer the observed parachors likewise increase rapidly with temperature in the vicinity of the melting point and it seems likely that here also a higher and truer mean value would have been obtained had the measurements been extended to higher temperatures.

EAST GRIMSTEAD
SALISBURY
WILTS, ENGLAND
S. A. MUMFORD
J. W. C. PHILLIPS

RECEIVED NOVEMBER 6, 1930
PUBLISHED DECEMBER 18, 1930

PARACHORS OF ISOMERIC CHLORODINITROBENZENES

Sir:

Through the courtesy of the Editor, we are enabled to add in this issue a few words on the subject of the foregoing interesting note.

In Table V of their cited article, Mumford and Phillips tabulate 361.2 under the caption "Σ At. P." and −8 under the caption σ (or strain constants). Since the strain constants for the nitro group are not referred to until two pages later, we had not understood that these were included in the value 361.2, which we took to be a misprint for 367.2, the value for the sum of atomic and structural constants. The interpretation of the authors is, therefore, very welcome.

The reason we made our measurements in the temperature range 40–60° was because this was the range used by Müller, whose enormous discrepancy it was our primary purpose to examine.

In comparing the results of Jaeger for the other isomer, we thought it fairest to use the portion of his temperature range closest to 40–60°; and, because we noticed that there was an apparent drift of this parachor with temperature, we corrected the value for drift in order to make the best possible comparison. When a parachor exhibits such drift, the best criterion for its absolute value is, of course, debatable.

DEPARTMENT OF CHEMISTRY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY
D. V. SICKMAN
ALAN W. C. MENZIES

RECEIVED NOVEMBER 14, 1930
PUBLISHED DECEMBER 18, 1930

THE STRUCTURES OF THE ACETYLMETHYLMANNOSIDES[1]

Sir:

Three new crystalline hepta-acetyl-4-glucosido-methyl-mannosides have been prepared by the Koenigs and Knorr reaction: (a) m. p. 185°, $[\alpha]_D^{20}$ $+26.7°$ in chloroform; (β) m. p. 161°, $[\alpha]_D^{20}$ $-22.3°$ in chloroform; (γ) m. p. 167°, $[\alpha]_D^{20}$ $-12.7°$ in chloroform. These new compounds appear to be analogous to the three previously known acetylmethylmannosides whose structures have been the subject of considerable controversy [Hudson, THIS JOURNAL, 52, 1680 (1930)]. Since the new compounds cannot contain a 1,4-ring, that ring structure is eliminated for compounds of the corresponding types. The new derivative designated "γ" exhibits the reactions characteristic of the acetylmethylglycosides which have recently been assigned an ortho carbonic ester structure by Bott, Haworth and Hirst [*J. Chem. Soc.*, 1395 (1930)] and also independently by K. Freudenberg [*Naturwissenschaften*, **18,** 393 (1930)].

The writer has found that the methoxyl group in one of his new compounds (γ) may be replaced by a hydroxyl group, giving a hepta-acetyl-4-glucosido-mannose, which does not exhibit mutarotation, $[\alpha]_D^{20}$ $+21.7°$ in chloroform. If the methoxyl group in the parent glycoside were combined directly with the first carbon atom upon removing the methoxyl group, the first carbon would be left free and the new substance would exhibit mutarotation. The absence of mutarotation for the new substance indicates that the methoxyl group in the parent hepta-acetyl-4-glucosido-y-methylmannoside was not combined directly with the first or aldehydic carbon. Thus the newly found reactions support the Haworth–Freudenberg ortho carbonic ester structure rather than the 1,3-ring structure for compounds of this type.

POLARIMETRY SECTION
BUREAU OF STANDARDS
WASHINGTON, D. C.

H. S. ISBELL

RECEIVED NOVEMBER 24, 1930
PUBLISHED DECEMBER 18, 1930

THE ACTIVATION ENERGY OF ADSORPTION PROCESSES

Sir:

A rapid development in experimental researches, during the last decade, on adsorption phenomena at solid surfaces having catalytic activity has served to emphasize the existence of adsorption processes in which a high degree of specificity is manifest. This has centered attention on the function of valence forces in determining adsorption. The experimental work has produced a number of results which, from the standpoint of classical adsorption theory, are abnormal. These include abnormal

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[1] Publication approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.

variations of the extent of adsorption with temperature and pressure, abnormal variations of the heats of adsorption with temperature and pressure, large variations in the velocity of attainment of adsorption equilibrium in different systems and in the velocity of evaporation of adsorbed gases. These several factors also influence the velocity of chemical processes occurring at the surfaces in question.

It has now been found that all of these difficulties can be removed and a unified method of treatment results once it is grasped that adsorption processes, in general, require an activation energy. It can be shown that the activation energies of such adsorption processes may vary from very small values to magnitudes such that the adsorption phenomena may first be obtained at quite high temperatures. Moreover, the magnitude of the activation energy is determined not only by the adsorption process in question but also by the nature of the surface area on which the process occurs. Thus, for example, the adsorption of hydrogen on the most active areas of catalytic metals involves such a small activation energy that the process is rapid at temperatures as low as $-100°$. With various oxide surfaces the adsorption process only manifests itself at temperatures several hundred degrees above room temperature. Numerous examples of these factors involving a variety of surfaces and the gases hydrogen, oxygen, nitrogen, carbon monoxide and water vapor as adsorbates have been collected. The detailed discussion of the subject will be communicated shortly.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY, N. J.
HUGH S. TAYLOR

RECEIVED DECEMBER 1, 1930
PUBLISHED DECEMBER 18, 1930

NEW BOOKS

Tables annuelles de constantes et **données numériques** de **chimie,** de physique, de biologie et de **technologie.** (Annual Tables of Constants and Numerical Data Chemical, Physical, Biological and Technological.) Published under the auspices of the International Research Council and the International Union of Pure and Applied Chemistry by the International Committee appointed by the Seventh Congress of Applied Chemistry (London, June 2, 1909). Vol. VII, Parts 1 and 2, 1925–1926. McGraw-Hill Book Company, Inc., 370 Seventh Ave., New York, 1930. Part 1, xxxv + 946 pp. Part 2, xv + 950 pp. 22.5 X 28 cm. Price, $25.00 per set.

All workers in the natural sciences will welcome the appearance of this double volume of the Annual Tables covering the years 1925–1926. Naturally the arrangement and mode of treatment followed in the earlier volumes are retained here. There are, however, certain minor changes and additions. English versions of some portions of the French text which might present some difficulties to the reader have been introduced. Two new chapters on Explosions and on Explosions in Gaseous Mixtures have been added and two old chapters treating of Photography and Geophysics have been omitted, since the specialists in charge of these subjects prefer to have them published only once in every two volumes. Numerous detailed indices to the substances mentioned in the tables and to memoirs whose data are not susceptible of inclusion in the Tables have also been added.

Dr. Marie, Secretary of the International Committee, announces that Volume VIII covering the years 1927 and 1928 is already in press and should be published by the beginning of 1931. With the next volume thereafter (Volume IX) covering 1929, the yearly publication of the Annual Tables will be resumed. Dr. Marie also calls attention to the forthcoming General Index covering Volumes I–V and this in the meantime has appeared.

These tables impress one with the beneficient results which can flow from an international cooperative effort of this kind entrusted to intelligent and public-spirited men.

ARTHUR B. LAMB

Non-Interpolating Logarithms, Cologarithms and Antilogarithms. By FREDERICK W. JOHNSON, M.A., Instructor in Chemistry, California College of Pharmacy, University of California. The Simplified Series Publishing Company. 1381 Third Avenue, San Francisco, California, 1930. 16 X 21.5 cm. Price, $1.60.

Five years ago no one would have considered that tables of logarithms offered much scope for any significant improvement. Nevertheless, within that period the graphical tables of Lacroix and Ragot [THIS JOURNAL, 48, 842 (1926)] have appeared and now we have these new tables of four- and five-place logarithms where, within substantially the compass of ordinary tables, logarithms (and antilogarithms) to four and five places, respectively, can be read off by inspection, without any calculation whatever. This is achieved very simply by the ingenious use of a new vertical arrangement and a mixture of bold-faced and ordinary type.

There seems to be no doubt in the case of the five-place logarithms that the new tables save both time and mental effort as compared with the ordinary tables. Moreover, it is not difficult to learn how to use them. In the case of the four-place logarithms the advantages are less pronounced. The elimination of interpolation is of less moment here, because anyone who uses frequently an ordinary four-place table can make the interpolations very quickly and easily. Moreover, the somewhat greater complexity of the new tables is here a noticeable drawback.

There is less to choose between these new tables and the above-mentioned graphical tables. So far as speed is concerned they are about on a par, at least for *a* person equally familiar with both. However, the mental effort involved in the use of the graphical tables, where one must correlate the two abutting scales to obtain the last two figures seems greater than in the use of these new tables.

There are also included in this volume the usual introduction, several pages of conversion factors, trigonometric functions and formulas and a table of "International Atomic Weights." This table besides being out of date (1925) gives logarithms of atomic weights to five places, irrespective of the number of significant figures in the atomic weights themselves.

Anyone who has to use five-place logarithm tables frequently would do well to give these tables a trial.

ARTHUR B. LAMB

Einführung in die technische Behandlung gasförmiger Stoffe. (Introduction to the Technical Methods of Handling Gaseous Materials.) By W. BERTELSMANN, Dipl.-Ing. Dr. phil., and F. SCHUSTER, Dr.-Ing. Verlag von **Julius Springer,** Link-strasse **23–24, Berlin W 9, Germany, 1930. x + 411 pp. 288 figs. 15.5 × 24 cm. Price, unbound, RM. 38; bound, RM. 40.**

The authors state that their book was written for the purpose of acquainting technologists in various fields with the methods technically employed in the generation, handling and purification of gases.

In the introduction (40 pages) an attempt is made to explain and summarize the physical-chemical laws which govern the behavior of gases and the reactions which occur in gaseous systems. Some of the material in this introduction is so elementary that the authors would have been justified in assuming that it would be familiar to the reader The discussion of the more important topics is so condensed that it would be of but little value to a reader who was not already familiar with these topics. The lack of clearness and completeness in the introductory chapter is not, perhaps, a very serious defect, since in the subsequent chapters of the book little reference is made to the underlying theory developed here.

Chapter I, on Warming, Cooling, Compression and Liquefaction of Gases, contains a rather elementary and descriptive discussion of these subjects. The general equation for the rate of flow of heat by conduction is given, but the reader will find little information as to the actual rates of heat transfer to be expected in any specific case.

The second chapter, on the methods for obtaining gases, includes a rather detailed description of the procedure followed in drilling for natural gas. To the reviewer, this topic does not appear to have sufficient general interest to justify the emphasis placed upon it here. The discussion of the fractional distillation of liquefied gases is so elementary and incomplete that it would be of little assistance to the reader who desired to gain even a general knowledge of this subject.

The third, fourth, fifth, sixth and seventh chapters deal with the preparation, purification, measurement, storage and distribution of gases, respectively. The treatment is largely descriptive.

The eighth chapter, on methods of testing and analyzing gases, is **very**

incomplete. Many of the methods and types of apparatus described therein are obsolete. Many of the newer methods actually used in the industries are not described.

In their attempt to cover a wide field in a single volume, the authors have omitted much which would be of great importance to any technologist who is called upon to prepare or handle industrial gases. In the opinion of the reviewer, the material which has been included has not been well selected nor ably presented. The reviewer does not regard this book as a particularly valuable contribution to the technology of gases.

F. H. RHODES

Lehrbuch der organischen Chemie. (Textbook of Organic Chemistry.) By Professor Dr. JULIUS SCHMIDT, Stuttgart. Fourth revised edition. Ferdinand Enke Verlag, Stuttgart, Germany, 1929. xxxvi + 896 pp. 17 figs. 16 × 25 cm. Price, unbound, RM. 4.5.50; bound, RM. 49.

In reviewing so compendious and so excellent a volume as this, one may dismiss the whole matter with a mere word or two of unstinted praise, or proceed to comment on the features good or otherwise. If the latter seem numerous it is only because space forbids the mention of all the good points and the relation between the acceptable and the unacceptable statements in the book is thus not accurately indicated.

The third edition of this splendid text, running to about 800 pages, was called a "Short Textbook." In closer accord with the facts, the present edition, the fourth, 850 pages, has had the adjective dropped from the title, a most pleasing change. The additional pages have permitted the inclusion of much new material as well as an amplification of the biochemical accomplishments of recent years, and have greatly increased the value of the book. The literature references, numerous and well-selected, are also surprisingly up-to-date, publications appearing as recently as 1929 being mentioned. This volume has very good author and subject indices, and the mechanical features of the book's production have been handled in the usual excellent manner of the Enke press.

As in the earlier editions there still appears, in the first part of this book, too much, and some quite superfluous, freshman chemistry; *e.* g., (p. 14) the method of calculating the empirical formula from the analytical results is given in detail. The distinction between an empirical and a molecular formula (p. 16) is not so clearly made as is desirable. It is a poor compliment to the prospective readers of this book that the author felt called upon (p. 29) to take a short section for an explanation of just what constitutes an hydroxyl group.

In discussing the cause of optical activity (p. 44), too much stress is laid on the presence of an asymmetric carbon and too little attention is devoted to the really essential feature, namely, that the molecule shall be asymmetric. A quite needless statement concerning the existence of compounds with water of crystallization (p. 66) is given, and Fig. 17 (p. 68), showing a flask with contents, presumably ready for distillation, indicates the thermometer improperly located. The diagram serves no real purpose in a book of this character. The statement (p. 82) to the effect that monovalent hydrocarbon radicals, aliphatic as well as aromatic, are generally called alkyls is not in line with general American practice at least. It is pleasing to note that the text mentions the members of the paraffin series higher than $C_{60}H_{122}$, since such compounds, though known for some years, are rarely referred to even in supposedly modern texts. It is certainly regrettable that the astonishingly incorrect statement, at least so by inference (p. 91), that Pennsylvania is still the center of the American petroleum industry, should have been permitted to remain in this new edition. The bad impression left with the reader by the foregoing is, however, promptly eliminated by the pleasure in finding the structure of phytol correctly presented. All too few writers have as yet become really aware of the beautifully conclusive work of F. G. Fisher with this interesting and important substance.

One is rather surprised that, under the topic of fat syntheses (p. 189), he finds no mention of materials with an odd number of carbon atoms in the acid chain; this is especially so in connection with this book because the medical aspects of most of the subjects are splendidly presented. The formula for pelargonic acid (p. 194) has a subscript written as an exponent. This slip in proofreading makes the text combine French and German practice. This unintentional stressing of the international aspect of chemistry may, however, be pardoned when one appreciates that this volume is very well supplied with formulas among which are discoverable surprisingly few typographical errors. In the discussion of dynamite (p. 250) reference is still made to the use of infusorial earth with no mention of the fact that wood powder, at least in this country, has long since replaced it.

The introductory statements under carbohydrates (p. 297) indicate that they "unquestionably" occupy first place in the study of foodstuffs. Without meaning to quibble too much, it might be pointed out that, in the absence of proteins, the carbohydrates, important as they are, are still insufficient for the continuance of life. The state of flux that still lingers in the minds of many concerning the nature of the cyclic forms of the hexoses is fairly presented by Schmidt.

In certain equations (p. 347) elementary diatomic gases are indicated without subscripts. As long as coefficients are required, and given, in the equations as presented, there seems to be no good reason why these gases should not be written to conform with common practice. Disodium malonic ester is to be found (p. 369), under the synthesis of a group of ring compounds, with two sodium atoms on the same carbon. Doubtless this formula is so given merely for convenience, but at least a word to indicate that the formula does not represent the accepted views would not come amiss. In this same section compounds are sometimes named, and referred to, in one place on the polymethylene basis and elsewhere the cycloparaffin nomenclature is used. It is to be hoped that in subsequent editions the author will adopt whole-heartedly the latter and more generally accepted naming scheme.

A rather surprising failure to indicate a modern advance in the field of industrial organic chemistry is shown (p. 436) by the appearance of the hoary statement to the effect that halogen on the aromatic nucleus cannot be replaced by hydroxyl by the action of alkali. The Dow phenol process is a daily, and important, refutation of this contention. Perhaps only purists would interpret "artificial camphor" to mean a substance resembling camphor in some of its properties, but not the same structurally, whereas "synthetic camphor" would be taken to mean *camphor* prepared by laboratory methods. If, however, this view is adopted generally by chemists, and many hold it, Schmidt's objection to the term "artificial camphor" is not so potent, or so well taken, as it might be.

The writer is happy to report that here is a text, the first seen by him at any rate, which presents the latest developments of the Beckmann rearrangement, including the *trans* shift. Meisenheimer's work with the oximes of benzil is also included.

The presentation of the subject of alkaloids is more than adequate, and quite unusual in a book of this type; approximately 75 pages are devoted to this important subject. Though the treatment of proteins is very well done, one is rather surprised to note no mention of Svedberg's ultracentrifugal method for determining the molecular weights of these substances. The section devoted to the structure of proteins has been very carefully prepared, and each of the important theories has received considerate attention.

This is an admirable text as far as book-work, content and manner of presentation are concerned—and there is not much more that can be said for a text.

G. ALBERT HILL

ADDITIONS AND CORRECTIONS

NOTICE TO READERS.—For the convenience of those who may wish to cut out the corrections and attach them to the margins of the articles corrected, they have been printed only upon one side of the page, and with ample space between each item.

1928. VOLUME 50

The Tautomerism of Brilliant Cresyl Blue, by Walter C. Holmes.

Pages 1989–1993. The author has supplied an explanatory correction: "The violet coloring matter which was isolated from an acid aqueous solution of cresyl blue by means of chloroform is not, as was mistakenly assumed, the violet tautomer of the dye which is present in aqueous solutions in increasing proportions as the dye concentration is increased. This is proved conclusively by the fact that it may not be thus isolated from other samples of the dye of different manufacture. It has been shown to be a subsidiary coloring matter which may, or may not, be present in varying small proportions in cresyl blue.

"It appears probable, as was suggested to the writer by Barnett Cohen, that the violet dye which is extracted with chloroform is an oxazone compound formed through the displacement of the free amino group in cresyl blue by oxygen. It has long been recognized that this type of hydrolysis occurs with naphthophenazoxine derivatives It has been claimed that it does not occur with diphenazoxine derivatives, of which cresyl blue is an example, but evidence has been obtained that this conclusion is mistaken."—W. C. HOLMES.

1929. VOLUME 51

Kinetic Studies on Ethylene Oxides, by J. N. Bronsted, Mary Kilpatrick and Martin Kilpatrick.

Pages 428–461. The following statement has been transmitted by Dr. Lennart Smith: "In an article by J. N. Bronsted, entitled 'Kinetic Studies on Ethylene Oxides,' published in THIS JOURNAL, 51, 428 (1929), there is the statement on page 431: 'After the present investigation was begun, Smith, Wode and Widhe published measurements on the rates of addition of water to ethylene oxide and to epichlorohydrin at 25° in solutions . . .'

"This statement is incomplete and for that reason misleading. These results were presented in preliminary form in lectures before the Chemical Society at Lund in the autumns of 1923 and 1924, and were reviewed in *Sv. kem. tidskrift*, **36,** 4 (1924), and 37, 30 (1925). In May, 1925, I delivered a summarizing lecture at Copenhagen, where all of the numerical material concerning the ethylene oxides was included. Professor Bronsted attended this last-mentioned lecture and was the first to speak in the discussion of it."—LENNART SMITH.

1929. VOLUME 51

The Heat of Adsorption of Oxygen on Charcoal, by Melville J. Marshall and Harold E. Bramston-Cook.

Page 2024. "The disagreement between some of the data in Table III and the curve in Fig. 3 is not caused by an error in the data, but is due to the fact that, after the curve had been drawn, slightly more accurate values of $-dc/dQ$ were substituted in that region of the table above Q = 69,800 calories. The extent of the error produced

in the curve by the large difference at Q = 70,000 calories is illusory, as, according to the curve, the values of Q corresponding to the two discrepant values of $-dc/dQ$ differ by less than 1%, due to the almost infinite slope of the curve at this point."—MELVILLE J. MARSHALL.

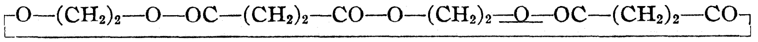
Salts of Triphenylselenonium Hydroxide, by Henry M. Leicester and F. W. Bergstrom.

Page 3590. In line 4 from the top, for "Eighty grams" read "Thirty grams."—HENRY M. LEICESTER.

1930. VOLUME 52

Studies on Polymerization and Ring Formation. IV. Ethylene Succinates, by Wallace H. Carothers and G. L. Dorough.

Page 718. Formula (IX) should read



$$-O-(CH_2)_2-O-OC-(CH_2)_2-CO-O-(CH_2)_2-O-OC-(CH_2)_2-CO-$$

WALLACE H. CAROTHERS.

Allene and Methylacetylene Tetrabromides by Charles D. Hurd, R. N. Meinert and L. U. Spence.

Page 1144. The designations R and S in Fig. 3 should be reversed.

The Synthesis of Some Iodated Diphenyl-Sulfide Phenols, by Shailer L. Bass and Treat B. Johnson.

Page 1150, line 13 from the end, for "$C_{12}H_8O_5I_2$" read "$C_{12}H_8O_5SI_2$."

Page 1151, line 25 should read, "*Anal.* Calcd. for $C_{12}H_8OSI_2$: I, 55.92; S, 7.06. Found: I, 55.8; S, 6.8."

Page 1151, line 29 should read, "*Anal.* Calcd. for $C_{13}H_{10}OSI_2$: I, 54.2; S, 6.85. Found: I, 54.6; S, 6.90."—TREAT B. JOHNSON.

The Action of Diazomethane on Some Aromatic Acyl Chlorides. V. The Mechanism of the Reaction, by T. Malkin and M. Nierenstein.

Page 1506, last text line, for "1772" read "1335."—M. NIERENSTEIN.

Relations between Rotatory Power and Structure in the Sugar Group. XXVI. The Ring Structure of Various Compound Sugars, by C. S. Hudson.

Pages 1717–1718. The structural formulas for sucrose, raffinose and gentianose should be corrected by the removal of the symbol H attached to the second carbon atom of their fructose portions.—CLAUDE S. HUDSON.

The Micro Determination of Halogens and Metals in Organic Compounds, by H. H. Willard and J. J. Thompson.

Page 1894, line 32, for "decomposition" read "absorption."—H. H. WILLARD.

Studies on the Polymethylbenzenes. III. The Vapor Pressures of the Tetramethylbenzenes and of Penta- and Hexamethylbenzene, by F. H. MacDougall with Lee Irvin Smith. ■

Page **2000.** In the last line of the caption of Fig. 2, for "added" read "subtracted."

Precision Actinometry with Uranyl Oxalate, by Wesley Glick Leighton and George Shannon Forbes.

Page **3141,** line **29,** for = read $\leqq$.

Page **3144,** line **18,** for "this case" read "the last case"

Page **3144,** line **35,** for $(I)_2$ read $(I_0)_2$.

Page **3148,** Fig. **1,** interchange the letters B and C on the curves so marked.

Page **3150,** line **19.** for "Table III" read "Table IV."

Page **3151,** Fig. **2.** The arrows designated I_0 should penetrate the right-hand wall.

Page **3152,** line **14,** read "**. . .** in spite of the fact that sodium sulfate and sodium hydroxide enhance total absorption. Sulfuric acid strongly reduces absorption."

Page **3152,** line **14,** for **"1.03 4 0.036"** read **"1.03** ± 0.025."—GEO. **SHANNON FORBES.**

Studies on Reactions Relating to Carbohydrates and Polysaccharides. **XXIX.** The Constitution of Alkali Cellulose, by Edmund G. V. Percival, **A.** C. Cuthbertson and Harold Hibbert.

Page **3260,** line 3, for "1.75" read "1.65"—**HAROLD HIBBERT.**

The Arsonation **of** Aromatic Aldehydes, by Albert B. Scott and Cliff S. Hamilton.

Page **4122,** Footnote **3,** the patent number should be **220,668** instead of 220,688.

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